DIFFUSION IN SOLUTION.

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Einstein[1] has shown that the relation between molecular movement and diffusion may be expressed by the following equation, when the particles move in--dependently of each other:

$$D = \frac{\bar{\Delta}^2}{2t} \qquad (1)$$

where D is the diffusion constant, and $\bar{\Delta}^2$ is the mean square of the deviation in a certain direction in time t.

Further, if it be assumed that the particles possess the same mean kinetic energy as a gas molecule at the same temperature, the following equation holds:

$$\bar{\Delta}^2 = \frac{2RT}{N} \cdot \frac{t}{c} \qquad (2)$$

where R is the gas constant, N Avogadro's number, T the absolute temperature, and C a constant which we might call the frictional resistance of the molecule. Hence:

$$D = \frac{RT}{N} \cdot \frac{1}{c} \qquad (3)$$

Under the foregoing assumptions equations (2) and (3) hold equally well for dissolved molecules and particles of greater dimensions.

(1) Ann.d.Physik.(4) 17,549(1905); 19,371(1906). Zeitschr.fur Elektrochemie, 14, 235 (1908).

Now, for spherical particles moving in a medium of proportionately small molecules, Stokes has shown that a hydrodynamic relation holds,-namely:

$$C = 6\pi Z r \qquad (4)$$

where r is the radius of a diffusing particle, and Z is the viscosity of the diffusion medium.

By substitution in (3) we obtain for D the following relation:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi Z r} \qquad (5)$$

This is known as the Stokes-Einstein equation, and is valid only when the aforementioned conditions are fulfilled.

Equation (5) has been experimentally verified for the diffusion of the comparatively large particles of suspensoids. Within recent years attempts have been made to test its validity for diffusing molecules. This has been done in a number of ways.

Method 1:-

The diffusion constant is determined for different substances, in the same solvent, at constant temperature, and r is calculated on the assumption that Dr is constant. The value of r can be ascertained by other methods, and a comparison drawn.

The Svedberg[1] found for the radius of the molecules of some organic substances values which at least roughly agree with our views of chemical structure. Öholm[2] doubted the validity of the equation.

Method 2:-

The influence of temperature is investigated for the same substance diffusing in the same solvent. J.D.R. and F.E.C.Scheffer[3] investigated the diffusion of mannitol in water for temperatures between 0°C. and 70°C.,and found that equation (5) is valid within the limits of experimental error. More recently Cohen and Bruins[4] determined the diffusion coefficients of tetrabromethane in tetrachlorethane at temperatures between 0°C. and 50°C. They concluded that there is a deviation from equation (5), in the sense that the temperature coefficient of the speed of diffusion is less than is to be expected.

Method 3:-

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(1) Zeitschr.f.physik.Chemie 76, 145 (1911).

(2) Meddel.Nobelinst. 2, Nr.23, (1913).

(3) Proc.Kon.Akad.v.Wet.te Amsterdam 19, 148 (1916).

(4) Zeitschr.f.physik.Chemie 103, 404 (1923).

Method 3:-

The diffusion constant of a certain substance is estimated in different solvents at the same temper--ature. According to Einstein the product DZ should be constant.

Thovert[1] was probably the first to show that a remarkable relation exists between the diffusion constant of a dissolved substance, and the viscosity of the solvent. Investigating the diffusion of phenol in ten different solvents, he found that DZ varied between the values 92 and 99. Later, Thovert[2] examined the diffusion of one hundred and thirty organic sub--stances in water, methyl alcohol, and benzene, and found that the diffusion constant tends to vary inversely as the viscosity of the solvent.

Öholm,[3] studying the diffusion of organic sub--stances in water and ethyl alcohol, found that the viscosity coefficients of solutions of the different substances and their inverse diffusibilities give values which run practically parallel. Later,[3] he found/

1) C.R.Acad.Sc.t. 138, 481 (1904).

2) Ann.de Phys. 2, 415 (1914).

3) Meddel.Nobelinst. 2,Nr.24, (1913);2,Nr.26,(1913).

found that the product DZ for bromoform and glycerine diffusing in ether, acetone, benzene and various alcohols is not constant. The deviation he attributed to the varying degree of association of the dissolved substance, to combination of solvent with solute, or to non-fulfilment of the conditions required for the validity of equation (5).

Dummer [1] found that for a certain substance diffusing in different media the molecular radius does not remain constant.

Experimental data serve to show that great care must be exercised in the application of the Stokes-Einstein equation to particles of molecular dimensions. With regard to the relation between D and Z, it appears that variation in the value of D depends to a considerable extent on the variation of the viscosity of the solvent, but recent results indicate that the product DZ varies by an amount in excess of the experimental error. As the number of published results bearing on this point is comparatively small, it was suggested that experiments might be performed in order to study further the effect of varying viscosity on the diffusion of dissolved molecules.

Iodine was chosen as the diffusing substance, for the following reasons. It has/

(1) Zeitschr.f.anorg.Chemie 109, 31 (1919).

has a fairly high molecular weight, is soluble in a wide range of organic solvents, and is readily estimated. The diffusion of iodine has not been previously studied to any extent. Euler[1] quotes the values of the diffusion constant of iodine in water, benzene, and carbon bisulphide, but no details are given to indicate the accuracy of the results. Edgar and Diggs[2] found the diffusion constants of iodine in solutions of potassium iodide.

As solvents, organic liquids of varying chemical constitution were used. In addition, determinations were made of the diffusion constants of iodine in a number of aqueous salt solutions.

The following sections describe the experimental method adopted, and give an account of the results obtained.

(1) Wied.Ann. 63, 273 (1897).

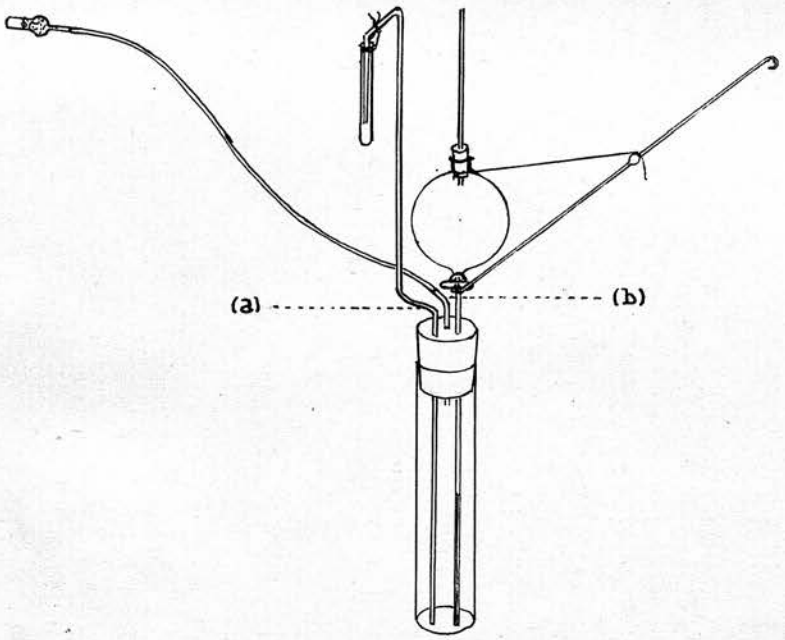
(2) Jour.Amer.Chem.Soc. 38, 253 (1916).

EXPERIMENTAL.

Diffusion Apparatus:-

Graham's second experimental method was adopted for the estimation of the diffusion constant. It consists in passing a definite volume of solution beneath three times that volume of pure solvent. After a certain time the liquid is removed in four equal por-tions which are reserved for analysis.

The apparatus used was very similar in form to Svedberg's [1] modification of Scheffer's [2] apparatus.



From time to time, as need arose, slight alterations were made, and the ultimate form was that shown in the diagram.

1) Zeitschr.f.physik.Chemie, 76, 145 (1911).

2) Zeitschr.f.physik.Chemie, 2, 390 (1888).

The diffusion tube was made from uniform glass tubing one and a quarter inches wide, and had a flat bottom. It was provided with a three-holed, tight fitting rubber stopper, through which passed a small tap-funnel and a long capillary tube (a), reaching to the bottom of the diffusion tube. A small tube (b) gave an atmospheric connection, and could be attached to a gasometer when it was desired to remove the liquid through (a), by displacement with air. The lower half of the stem of the tap-funnel was made of capillary tubing, and on to the stop-cock was fused a long handle which, when the apparatus was immersed, enabled one to turn the stop-cock without putting the hand in the water. A piece of string tied between the neck of the tap-funnel and the handle prevented the latter from falling back too far. A small rubber stopper with a long narrow glass tube was placed in the neck of the tap-funnel.

Entrance of water into the apparatus was pre--vented by attaching to the end of (a) a small tube, as shown, and to (b) a calcium chloride tube. When the apparatus was immersed in water only the air connection tubes and the top part of (a) were above the surface.

Steady Temperature Surrounding for Diffusion Apparatus:-

From the literature it is evident that steady temper--ature cellars are the most satisfactory places in which to perform diffusion experiments. As such a cellar was not available when this work was begun it was necessary to find a substitute. Unsatisfactory results were obtained when the diffusion apparatus were placed in boxes of sawdust, in baths of running tap-water, or in vessels in which constant temper--ature water was circulated.

Benzene, chloroform and carbon bisulphide were the chief diffusion media used for test experiments. In using organic solvents greater experimental difficulties are encountered than in the use of water, the reason being that the larger coefficients of expansion and lower specific heats of the former render them more susceptible to temperature changes.

Since one diffusion experiment yields normally four similar values for the diffusion constant, it was possible to tell whether or not an experiment was a success by noting the degree of variation of the four values obtained. In addition, owing to the deep colour of iodine solutions, one was readily able to observe the upward diffusion of iodine into the colourless solvent. In a satisfactory experiment, when /

when the tube was viewed from the side, the line of separation of solvent and solution remained perfectly straight; in a poor experiment the line became very uneven, and the pure solvent prematurely coloured with the iodine transported by disturbing currents.

No disturbing error of appreciable magnitude could be attributed to the time and method of addition of the iodine solution, nor to the time and method of removal of the four liquid portions. Different methods of addition and removal did not effect any improvement. The substitution of benzoic acid for iodine did not improve the results. The experiments were not affected by light. The disturbing features, therefore, could only be temperature change, or vibration, or both.

The apparatus were next immersed in a small air-stirred thermostat, but even with a temperature variation of only ·02°C. good results were not obtainable. Kawalki [1] has indicated that satisfactory results are not to be obtained by use of a thermostat, and other investigators have corroborated his state-ment. Despite these opinions the thermostat was further utilised.

It was found to be an advantage to fix the tubes in weighted, thick glass jars of water, kept in the bath. The effect of the jars was most probably to cut /

1) Wied. Ann. 52, 177 (1894).

cut down any temperature variations in the tubes. The diffusion apparatus were next surrounded by jars of air and cotton wool, or Dewar flasks kept constantly in the bath, but the results did not show the improve--ment expected. In such cases there was a greater tendency for small temperature changes to arise between solvent and solution, before the latter was run into the tube from the tap-funnel.

The effect of varying the thermostat temper--ature was studied in order to find if there was a certain temperature which rendered the thermostat an effective surrounding medium for diffusion tubes. The first excellent result was obtained when the temper--ature was kept low by the passage into the bath of a large quantity of cold water. The stirring was except--ionally vigorous and shook the diffusion tube, so that vibration could not hitherto have caused the bad results. Unfortunately, although further experiments were performed in exactly the same way, satisfactory results were only obtained at intervals. Results were very often poor on warm days, which seemed to show that the atmospheric temperature was affecting the experiments. Without the passage of cold water into the bath no satisfactory results were obtained. There was no doubt that the cold water exerted a highly beneficial effect. Probably certain combinations of the temperature /

temperature of the atmosphere, and of the temperature and amount of the cold water added, rendered the thermostat a suitable medium in which to perform diffusion experiments.

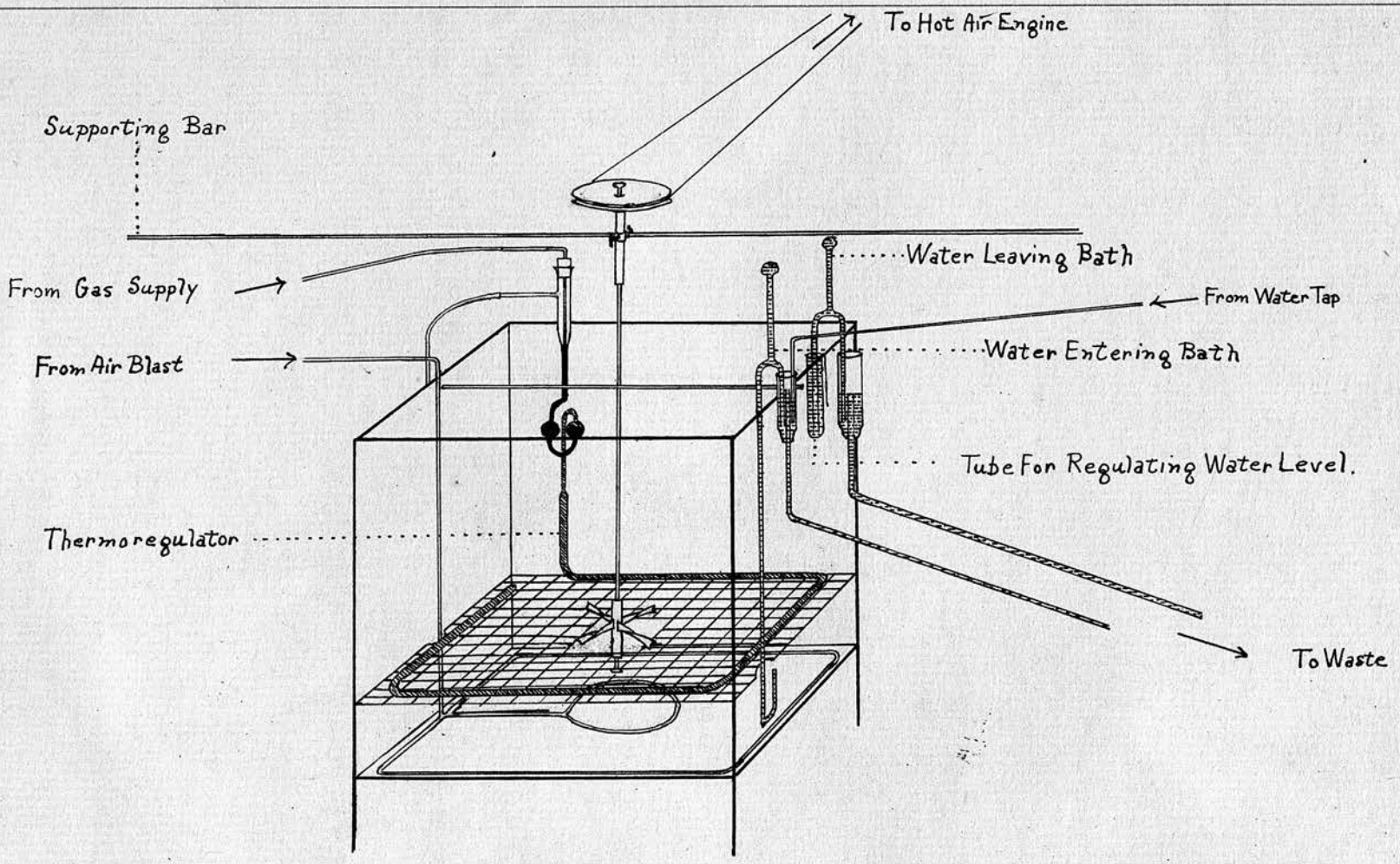
The starting point of an experiment was extrem--ely critical. If convection currents arose in the diffusion tube immediately after the addition of the iodine solution, the experiment rarely righted itself again. In some cases diffusion took place normally for four or five hours, and then convection currents arose, although the temperature variation in the bath was only .01°C. More concentrated iodine solutions, as was expected, gave slightly better results.

A considerable time was spent in testing the effect of different methods of heating the bath. In some cases the bath was heated at the top by gas. On the whole, the experimental results were neither better nor worse than with the customary heating from beneath. Strange to say, on one occasion when the stirring of the bath ceased overnight, a satisfactory result was obtained when the temperature at the top of the bath was 10°C. higher than at the bottom. No cold water was being passed into the bath. It seemed as if the temperature gradient were beneficial. Several attempts were made to obtain a minute temperature gradient in the bath by having the surface water warmer /

warmer than the water beneath. On a few occasions when such a temperature gradient was actually established, in a crude manner, experiments were greatly improved. No suitable method, however, could be evolved for obtaining a very minute temperature gradient, with constant temperature at any one level in the bath.

A much larger thermostat was fitted up, and will be described presently in greater detail.

In spite of excellent temperature control, satisfactory results were once more obtained with great irregularity. Again it was found to be advan--tageous to pass cold water into the bath. Good results were occasionally obtained systematically for one or two weeks, to be followed quite unexpectedly by series of bad results. In such cases a pronounced change in the atmospheric temperature was frequently noted. The larger thermostat, however, proved to be much more satisfactory than the smaller, and with the better temperature control,the experiments were as satisfactory when the tubes were placed directly in the bath as when they were protected by thick glass jars.


To Hot Air Engine
Supporting Bar
From Gas Supply
From Air Blast
Water Leaving Bath
From Water Tap
Water Entering Bath
Tube For Regulating Water Level.
Thermoregulator
To Waste

Thermostat and Equipment:- (See sketch).

The thermostat ultimately used was a two hundred litre copper bath, the inside of which was painted white. Nine inches from the bottom was a wire tray on which was supported a large thermoregulator which just fitted into the bath.

Originally the bath was stirred vigorously by means of compressed air which escaped from perforated composition tubing, arranged on the bottom of the bath. Latterly, owing to defective working of the air compresser, it became necessary to introduce a differ--ent method of stirring.

Mechanical stirrers of various types were tried. The most satisfactory was a brass paddle, consisting of four six-inch blades which were slightly twisted. Using power derived from a hot air engine, this paddle was driven, on an average, at the rate of one hundred and fifty revolutions per minute. It was found to be most advantageous to rotate the paddle just above the wire tray, and in the direction in which it forced the water down.

As vibration may upset the process of diffusion, the stirring gear was fixed entirely apart from the bath. Three feet from the bath the hot air engine was screwed to a small table, heavily weighted in order to avoid displacement and vibration. The bath was found to be free from vibratory disturbances.

Temperature Control of the Thermostat:-

As the temperature control of the thermostat was of extreme importance it is necessary to describe it in detail.

The thermoregulator, which had to be specially made, contained 650ccs. of chloroform which proved to be a thoroughly reliable liquid for the purpose. With vigorous stirring of the bath and freedom from sudden draughts, the temperature of the bath varied by an amount which was scarcely perceptible on a large Beckmann thermometer. The variation seemed to be $\pm$ .005°C. Owing, however, to increase of gas pressure in the main at certain periods of the day mercury spurted up in the thermoregulator, and adhered to the glass, thereby causing a rise of .1°C. in a night.

In order to combat the effect of variable gas pressure, a gas pressure regulator was specially designed by a member of the departmental staff.[1] After the installation of this apparatus no difficulty was experienced in maintaining temperature constant to .01°C.,not only for 24 hours, but for weeks at a time. Since, in using this pressure regulator, the heating is intermittent the effect might be compared with that produced by use of an electric thermoregulator desig-ned by Gouy[2], where /

1) Jour.Chem.Soc. 125, 461(1924).

2) Jour.Amer,Chem.Soc.Trans. 42, 60(1920).

where, in order to give greater sensitiveness, the platinum wire making contact with the mercury surface was given an oscillating movement along the axis of the capillary.

As previously stated, cold water was always passed into the bath near the foot and warm water removed at the surface. The amount of cold water added depended on the atmospheric temperature. During hot weather, when the room temperature sometimes exceeded that of the bath, it was necessary to add a consider--able amount.

The addition of cold water served three purposes. Primarily, it exerted a beneficial effect on the experiments; secondly, it kept the bath water clean; and thirdly, it caused constant circulation of water in the bath.

The thermostat was protected on all sides by sheets of asbestos. Latterly a special box of asbestos millboard was made to fit entirely over the bath. In this way a much more constant temperature was main--tained round the bath, and there was little danger of the bath temperature falling on excessively cold nights.

Volumes of Liquid Used:-

At the start of an experiment a diffusion tube con-
-tains four equal "layers" of liquid, of which the upper three are pure solvent. In all the experiments for which results are quoted later 10 ccs. constituted a liquid "layer". This choice was not arbitrary.

If large volumes of liquid are used analysis figures are more accurate, and errors due to slight unevenness in the bottoms of the diffusion tubes are rendered negligible. On the other hand, a great depth of liquid requires a longer time of experiment, with consequent longer exposure to disturbing influences, and inequalities of temperature at different parts of the liquid are more liable to occur. If, however, too small a volume be used there is inaccuracy in analysis, and inaccuracy in determining the height of a liquid layer, owing to surface tension effects.

In using 10 ccs. as the volume of a liquid layer it was thought that the unavoidable experimental error would be a minimum.

For measuring out solvents and solutions, a number of pipettes were carefully standardised to deliver the same amount. The volume was practically 10 ccs.

Calibration of Diffusion Tubes:-

It was necessary to determine whether or not the diffusion tubes were uniform, and to find exactly the height of a 10 cc. liquid layer, when the fittings of the tube were in position.

Calibration was effected in the following manner. The tube was firmly fixed in a vertical position, and 10 ccs. of mercury added. A piece of a Beckmann thermometer scale was inserted and just touched the bottom of the tube. Using a microscope, within which was a scale, the position of the mercury against the Beckmann scale was noted. Fractions of a Beckmann scale division were estimated, knowing the relation between Beckmann and microscope scale divisions. Errors due to parallax were carefully avoided.

Mercury was further added in three 10 cc. portions and readings again obtained. The difference between two successive readings represented the increase in height due to 10 ccs. of mercury. For all the tubes standardised the three values obtained for each tube were practically identical, a fact which showed that the tubes were uniform. The height of the 10 ccs. of mercury initially inserted was assumed to be the average of the heights of the other three layers.

The tap-funnel and long capillary tube were next inserted in position in the tube, and the increase in /

in height of the 40 ccs. of mercury noted. The de-
-crease in height due to the removal of the Beckmann scale was determined by means of the microscope scale. From the set of readings obtained it was possible to calculate $\underline{h}^2$, where $\underline{h}$ represents the height of half a layer of liquid, and is calculated in centimetres.

The following table gives the values of $\underline{h}^2$ obtained for the various apparatus.

Tube.	$\underline{h}^2$.
I	.6637
I_a	.6670
II	.6451
II_a	.6396
III	.6807
IV	.6579
V	.6740
VI	.6579
VII	.6797
VIII	.6454
IX	.6784
X	.6461
XI	.6779
XII	.6458

Solvents Used:-

It was desired to obtain the diffusion constant of iodine in as many organic solvents as possible. Experiments were therefore performed with the follow-
-ing liquids,- methyl and ethyl alcohols, ether, ethyl and amyl acetates, acetic acid, anisole, phenetole, pentane, heptane, benzene, toluene, m-xylene, chloro-
-form, carbon tetrachloride, carbon bisulphide, bromo-
-benzene, /

bromobenzene, ethylene dibromide and acetylene tetra--bromide. The solvents were purified where necessary,- for example, toluene was freed from thiophene and carbon bisulphide from sulphur. With the exception of acetic acid, all were dried in the customary manner, and distilled. Acetylene tetrabromide had to be distilled under reduced pressure.

Aqueous solutions of inorganic salts were also used as solvents for iodine. The salts chosen were the bromides and iodides of sodium, potassium and ammonium. These were thoroughly dried and made up in solutions of strengths one, two, three, and four normal.

Normality of Iodine Solutions:-

In the literature it is noted that fairly concentrated solutions have as a rule been used in diffusion exper--iments. Thus, Öholm[1] used chiefly normal and half normal solutions, and Dummer[2] 10% to 20% solutions. Thovert[3], however, used only 2% solutions.

More concordant values of the diffusion constant are obtained by the use of concentrated solutions, owing to the greater density difference between solvent and solution. Since, /

1) Meddel.Nobelinst. 2, Nr.26,(1913).

2) Zeitschr.f.anorg.Chemie 109, 31(1918).

3) Ann.de Phys. 2, 369(1914).

Since, however, the Stokes-Einstein equation pre-supposes a dilute solution of the diffusing substance, it is advisable to keep the concentration of the iodine solution as low as possible. With decreasing concentration of the diffusing substance, the diffus-ion constant tends to a limiting value. If, therefore, values of the diffusion constant are obtained at high concentrations, it is necessary to obtain the limiting value by extrapolation, a procedure which is not very satisfactory.

Accordingly, in the following experiments with organic solvents, the iodine solutions used were about .10 normal. In the case of the aqueous salt solutions the strength of the iodine was only .05 normal. In normal bromide solutions this had to be reduced further to .02 - .025 normal, owing to the slight solubility of the iodine.

Prevention of Leakage in the Stop-cocks of the Tap-funnels:-

It was necessary to ensure that there was no leakage of iodine solution through the closed stop-cocks, and to have the ends of the latter protected from the entrance of water.

When liquids insoluble in phosphoric acid were in use, a few drops of syrupy phosphoric acid were placed /

placed on the centre part of the stop-cock, and the end parts were smeared with vaseline. When using aqueous solutions the whole stop-cock was smeared with vaseline, and, when alcohols, melted rubber. The use of ethyl acetate as a solvent presented difficulties, owing to the readiness with which it dissolved vaseline, melted rubber, phosphoric acid and water. Calcium chloride solution was placed on the centre part of the stop-cock, but it was found that, when air displace--ment of the layers was in progress, iodine solution was forced through the stop-cock. A moderately concen--trated sugar solution was ultimately used. As before, the ends of the stop-cock were protected with vaseline.

Performance of Experiments:-

Solvent and solution were heated up to the thermostat temperature and 30 ccs. of solvent measured into a diffusion tube. The stem of the tap-funnel was filled with iodine solution, and about 10 ccs. allowed to run out of the bulb until the bulb was just empty. There--upon there were sucked into the capillary stem of the tap-funnel, first a small air-bubble, and then a length of about 5 cms. of pure solvent. The reasons for this were as follows. Experiment had shown that, when the stem of the tap-funnel was completely filled with iodine solution, iodine diffused prematurely from the foot /

foot of the stem, and, further, that when this occurr--ed, the experiment was very often a failure. By observing the air bubble it was also possible to regul--ate to a certain extent the rate of entry of iodine solution into the diffusion tube. The escape of the air bubble through the liquid had no disturbing effect.

With aqueous solutions it was better to have no air bubble in the stem of the tap-funnel, as the pressure necessary to dislodge the bubble caused the iodine solution to rush suddenly into the tube.

10 ccs. of a standardised iodine solution were next measured into the bulb of the tap-funnel. An extra drop was added to allow for the small quantity which later passed into the long capillary exit tube. After fixing in position the stopper and fittings of the diffusion tube, the whole apparatus was immersed as completely as possible in the thermostat, and the tube clamped in a vertical position.

The apparatus was left untouched for two, or more, hours, and then the iodine solution was run carefully under the pure solvent. The time taken was usually 5 - 15 minutes. Undue extension of the time did not appear to be a benefit, and it seemed that the speed of addition did not matter a great deal provided that the iodine solution passed smoothly under the solvent. Using a mirror in conjunction with the white-painted side /

side of the bath as a background, it was possible to observe with comparative ease the entry of the solution into the tube. After the installation of the mechanical stirrer it was unnecessary to cut off the stirring, even momentarily.

The apparatus was left in position until dif--fusion had proceeded to a stage which will be indic--ated when the tables used for calculating the results have been considered.

The next operation was the removal of the four liquid layers, by displacement with air.

The level of water in the bath was lowered to one half inch below the end of the long capillary tube, (a). On to the latter was slipped a 10 cc. standard bulb with a long narrow neck. The bulb was below the surface of the water, so that the liquid was collected at thermostat temperature. Along with the first 10 ccs. was collected the small amount of liquid in the capil--lary tube during the experiment. This amount had been determined, and a small correction was applied to the analysis figure. The time chosen to collect a layer was usually 5 - 10 minutes, but owing to the more viscous nature of some of the solvents this time was occasionally exceeded. When using fairly volatile solvents it was desirable to keep the time of collection short.

The amount of iodine in the layers was estimated with a solution of sodium thiosulphate, ten times weaker than the original iodine solution. With organic solvents insoluble in water, a slight excess of the thiosulphate was added and the two layers churned up with a special stirrer. An iodine solution half the strength of the thiosulphate was used for titrating back.

When the solvents employed were concentrated iodide solutions, alcohols, ether and ethyl acetate, the end points with starch were bad, but by diluting considerably quite satisfactory results were obtained.

The number of experiments simultaneously per-formed for one solvent was usually three, but occas-ionally it was two or four.

Table for Calculation of Diffusion Constant.

The value of the diffusion constant, D, was found with the aid of Kawalki's[1] modification of Stefan's[2] tables. For definite values of h^2/Dt, - where t denotes the time in days /

1) Wied.Ann. 52, 177 (1894).

2) Wien.Akad.Ber. 79(2), 161 (1879).

days,- are given the proportional amounts of dissolved substance in the four layers, when the total quantity is 10,000.

Hereafter h^2/Dt is denoted by X. The tables are given for values of X between 1.4400 and .0400. Below is given that section of the table which was required for the experiments under consideration. The four layers are denoted by the numbers I,II,III,and IV, where I refers to the uppermost or most dilute layer.

X.	I.	II.	III.	IV.
.1600	996	.1816	3097	4088
.1936	755	1660	3172	4411
.2304	563	1504	3217	4716
.2704	412	1350	3236	5001
.3136	300	1203	3230	5267
.3600	214	1063	3201	5516

Time Chosen for Diffusion Experiments.

Before performing diffusion experiments many points require consideration, e.g.

(1) The effect of making the time of experiment very short or very long.

(2) The effect of unevenness of the bottom of the diffusion tube.

(3) The effect of evaporation of solvent during the course of an experiment.

First of all, if the time of experiment be very short the values of X obtained are large, that is, the amount of the diffusing substance in layer I is very small, and, as a consequence, a slight accidental loss or gain of solute gives a value of X rather different from the values for the other three layers. From this point of view a longer time of experiment is better. It is not advisable, however, to prolong an experiment unduly, owing to the existence of many external dis--turbing influences.

Secondly, if the bottom of the tube be uneven and the value of h^2 for layer IV accordingly slightly different from the average determined from the other three layers, there will be an error in estimating the diffusion constant. Since this error increases as the concentration of solute in layer IV decreases, the time of experiment should be short.

Lastly, since the amount of evaporation of solvent increases with time, the time of experiment should be short.

On the whole, therefore, it seems that the time of experiment should be kept as short as possible.

An endeavour was made to obtain for the various experiments values of X between the limits .32 and .19, and,in the case of the more volatile organic solvents, values /

values preferably above .23. The reasons for this choice were as follows.

Since convection currents always increased the amount of solute in layer I, it was inadvisable to choose a value of X exceeding .32. Next, by consider--ing Stefan's tables for a sixteen layer system, the effect of loss of solvent was calculated. For 1 cc. evaporation it was found that, within the above limits, the average value of D for the four layers would remain almost constant, although the actual values for layers I and II would be decreased and increased respectively. In most of the experiments performed the loss of solvent by evaporation was less than 1 cc.

Calculation of Results.

The relative amounts of solute found by analy--sis for the different layers enabled one to determine, for each experiment, four values of X. Since X does not vary linearly with concentration, intermediate values of X were found by graphic interpolation. For this purpose two large curves were drawn for each layer, the first for values of X between .1600 and .2304, and the second for values between .2304 and .3136.

Since the values of $\underline{h}^2$ were known, it was only necessary to determine $\underline{t}$, which differed slightly for different layers.

The Value of t for Different Layers:-

The starting point of an experiment was, of course, the moment that the iodine solution started to pass under the pure solvent.

Since the time of collection of the layers was short, it was assumed that diffusion from one layer to the layer above continued normally during the removal of the former.

For layer IV the time of experiment was until the beginning of removal of layer III, and for layer I until the beginning of removal of layer I.

In the case of layer II the end point was taken as the beginning of removal of that layer. After the removal of layer III, and during its own removal, II continued to lose iodine to I, but ceased to make good the loss,- that is, the iodine content of II was decreasing with time instead of increasing, as is normally the case. This made X greater than it ought to have been,and therefore, to counteract this, the smallest value of t was taken. Arguing in a similar manner the end point for layer three was the same as for layer II when the iodine content was normally decreasing with time, and the same as for layer IV when the iodine content was normally increasing.

Four values of D were thus obtained for each experiment. It was then necessary to calculate from these a mean value, taking into account the fact that they were not of the same relative importance. The most important layer is IV, since, in it, the value of X changes least for a certain change in the iodine content.

Kawalki and later investigators determined the mean D value in the following way. They multiplied D for each layer by the theoretical change P in the quantity of solute, determined from tables, between values of X directly above and below the X value obtained by experiment. The sum of the four products was thereupon divided by the sum of the four P values, giving the final value of the diffusion constant.

This method of obtaining a mean value of D was not considered entirely satisfactory for the majority of the experiments of which the results are quoted on page

First of all, for a perfectly normal diffusion experiment, the four D values ought to be the same. Owing, however, to the many disturbing influences this was rarely the case.

It was found that, for a number of experiments with a given solvent, layer IV usually offered a fairly constant value for D, in spite of great irregu-larity in the values given by the other layers.

Even in experiments in which there existed a variation of 20% between the D values of layers I and II, the value for layer IV was much the same as that given by a thoroughly satisfactory experiment. It was assumed, therefore, that when diffusion did not proceed too far and the variation between the values of D for layers I and II was under 20%, the value for layer IV was approximately correct. As the iodine content of layer III varied very slightly with change of X, for values of X between .19 and .32, the D values of that layer were usually somewhat different from those of the other layers.

The following changes were made in Kawalki's method of estimating the mean value of D.

1) Instead of finding P for the X value of the layer under consideration, P was determined, for each layer, for the supposedly normal value of X given by layer IV. Disturbing influences caused deviations from the normal values of X, but it was the P values of these normal values which indicated the relative importance of the layers.

2) Instead of taking the same P values for all values of X between say, .2704 and .2304, curves were drawn showing the variation of P with X. P was taken for a difference in X of .01. From the curves a definite P value was obtainable for every value of X. By deter-

-mining P for layers /

layers I,II,and IV for a given value of X, the P value of layer III was calculable. As the rate of change of P with X was greatest for layer III, more accurate values were obtained, in particular, for this layer.
3) On scanning the tables of results it is noted that in 80% of the experiments the D value of layer III is greater than that given by layer IV. Had errors of analysis been the sole cause of the varying values one would have expected to find the value for layer III as often less as greater. Convection currents, however, were much more likely to be responsible for the discrepancies, and for moderately satisfactory experiments they affected layers I,II, and III. Layer III lost iodine which was gained by layers I and II. For values of X below .275, the loss of iodine in layer III caused a decrease in X and consequent increase in the normal D value. The gain of iodine in layers I and II caused once more a decrease in X and increase in D. In other words, the two effects did not counteract each other as would have been, to a certain extent, the case had iodine been lost simply from II to I. As so many experiments were affected to a greater or less extent by convection currents, it was thought that a more nearly correct mean value of D would be obtained by subtracting the DP value for layer III from the sum of the other three, and dividing the resultant number /

number by the corresponding algebraic sum of P values.

When the normal value of X slightly exceeded .275, but layer III contained less than the normal amount of iodine there were two possible values of X, - see table, page 26. The lower value was, however, chosen. It was assumed that, since, normally, layer III would have contained almost the maximum amount of solute, disturbing influences had caused the maximum to be reached and passed.

There was no justification for the use of section 3) of the new method of calculation in those cases where convection currents had not arisen, and the chief error was probably one of analysis. It was difficult, however, to set a limit to its applicability, and, therefore, as its use appeared to be justifiable for the majority of the experiments, it was used for all.

With the most satisfactory experiments there was little difference in the results obtained by Kawalki's method and the new method.

Below are given, for purposes of comparison, a few examples of results worked out by both methods.

In the first column are the D values for layer IV. These are supposed to be very near the correct values. The second and third columns contain the mean D values worked out respectively by Kawalki's method and the new method.

a) Set of poor experiments:-

Methyl Alcohol:-

Exper. 1.	1.569	1.625	1.581
Exper. 2.	1.562	1.584	1.563
Average.	1.566	1.605	1.572

Benzene:-

Exper. 1.	1.670	1.679	1.667
Exper. 2.	1.672	1.698	1.672
Exper. 3.	1.670	1.710	1.670
Average.	1.671	1.696	1.670

b) Set of satisfactory experiments:-

Bromobenzene:-

Exper. 1.	1.035	1.034	1.035
Exper. 2.	1.043	1.037	1.041
Exper. 3.	1.039	1.037	1.038
Average.	1.039	1.036	1.038

In the case of b) it is seen that there is little difference in the results obtained by the two methods, but in a) the values obtained by the second method agree much better with the values in the first column than do those obtained by Kawalki's method.

Tables of Results.

At the head of each set of experiments are mentioned the solvent, the normality of the iodine solution and the temperature, which was the same for all experiments.

The numbers in brackets refer to the number of the experiment, and the Roman numerals to the appar--atus used.

The first column gives the relative proportions of iodine found in the layers in the order I to IV, where the total quantity was 10,000.

$X = h^2/Dt$, (obtained graphically), where h is half the height of a liquid layer and t is the time in days. Values of h^2, corresponding to the tubes used, are given on page 19.

D is the diffusion constant.

P has the significance already indicated, and was obtained from graphs for layers I, II, and IV, and by calculation for layer III.

$\overline{D}$ is the mean value of the diffusion constant, obtained as stated.

Table 1 refers to aqueous salt solutions as solvents for iodine,- Table 2, to organic solvents.

Only results of what were thought to be reliable experiments are quoted. In a number of cases it was, of course, only necessary to perform one set of exper--iments, but in others frequent repetition /

repetition was necessary before results were obtained, in which the four D values of a single experiment were in sufficiently good agreement. Originally it was hoped to have the variation between the values of layers I, II, and IV below 5% in all the results tabul--ated, but, owing to the great difficulty in obtaining even moderate values for some solvents, slightly less satisfactory experiments had to be included in the lists.

In the case of carbon bisulphide only one result is given, as it was apparently the best of a number obtained from rather poor experiments. Too much import--ance must not, however, be attached to it. No results are given for pentane, ether and ethyl alcohol, as all the experiments were failures. It is probable that a very slight reaction was going on in the case of ethyl alcohol, as isoamyl alcohol was found to absorb iodine.

The analysis figures are not given, as there was always satisfactory agreement between the total iodine values before and after analysis.

TABLE 1.

N. NH_4Br. .030N. I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	479	.2513	2.867	.896	353	316.3	
	1400	.2568	2.864	.878	377	331.0	.878
VIII	3206	.2186	2.864	1.031	30	30.9	
	4913	.2576	2.860	.876	700	613.2	
(2)	433	.2643	2.875	.893	322	287.6	
	1338	.2737	2.869	.864	366	316.2	.881
IX	3244	.....	.....	....	...	.....	
	4985	.2678	2.864	.884	674	595.8	
(3)	493	.2474	3.014	.866	413	357.7	
	1472	.2381	3.009	.902	394	355.4	.889
X	3248	.....	.....	....	...	.....	
	4787	.2401	3.005	.895	745	666.8	

2N. NH_4Br. .039N. I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	491	.2480	2.841	.965	334	322.3	
	1331	.2758	2.838	.868	370	321.2	.910
VII	3221	.2362	2.838	1.014	20	20.3	
	4957	.2638	2.834	.909	684	621.7	
(2)	457	.2573	2.844	.927	340	315.2	
	1358	.2680	2.840	.891	372	331.5	.910
IX	3237	.....	.....	....	...	.....	
	4948	.2626	2.835	.911	687	625.9	
(3)	475	.2524	2.891	.885	391	346.0	
	1459	.2414	2.885	.928	388	360.0	.909
X	3230	.2520	2.885	.889	51	45.3	
	4836	.2465	2.878	.910	728	662.5	

3N. NH_4Br. .044N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	450	.2592	2.711	.959	310	297.3	
	1337	.2741	2.707	.908	363	329.6	.923
V	3204	.2168	2.707	1.148	9	10.3	
	5009	.2716	2.704	.918	664	609.5	
(2)	438	.2626	2.731	.948	310	293.9	
	1338	.2737	2.727	.911	363	330.7	.921
VII	3212	.2245	2.727	1.110	9	10.0	
	5011	.2720	2.724	.917	664	608.8	

4N. NH_4Br. .044N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	556	.2321	3.094	.916	409	374.6	
	1448	.2443	3.091	.871	392	341.4	.885
VI	3199	.2128	3.091	1.000	59	59.0	
	4797	.2414	3.089	.882	742	654.5	
(2)	525	.2397	3.129	.906	395	357.8	
	1457	.2420	3.124	.899	389	349.6	.892
VII	3197	.2112	3.124	1.030	53	54.6	
	4821	.2449	3.120	.890	731	650.6	

N. NH_4I. .065N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	582	.2266	2.893	1.028	430	442.0	
	1470	.2386	2.887	.978	398	389.2	.994
V	3197	.2112	2.887	1.105	68	75.1	
	4752	.2354	2.881	.994	760	755.4	
(2)	517	.2416	2.622	1.010	393	396.9	
	1439	.2464	2.618	.992	388	384.9	.995
II_a	3213	.2258	2.618	1.082	52	56.3	
	4831	.2460	2.615	.994	729	724.6	

2N. NH_4I. .049N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	756	.1935	2.934	1.127	576	649.1	
	1604	.2064	2.930	1.058	436	461.2	1.098
II_a	3182	.1996	2.930	1.094	145	158.7	
	4458	.1990	2.926	1.099	867	952.7	
(2)	750	.1945	2.987	1.132	560	633.9	
	1603	.2066	2.980	1.069	432	461.8	1.092
VI	3161	.1874	2.980	1.178	135	159.0	
	4486	.2025	2.975	1.092	857	935.8	

3N. NH_4I. .049N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	645	.2136	2.681	1.177	485	570.9	
	1538	.2220	2.675	1.135	414	469.9	1.151
V	3189	.2050	2.675	1.229	94	115.5	
	4628	.2192	2.669	1.152	805	927.4	
(2)	713	.2011	2.739	1.173	536	628.7	
	1586	.2106	2.734	1.122	426	477.9	1.140
X	3172	.1936	2.734	1.221	122	149.0	
	4530	.2075	2.730	1.141	840	958.4	
(3)	746	.1952	2.763	1.186	560	664.2	
	1603	.2066	2.757	1.123	432	485.1	1.147
II_a	3161	.1874	2.757	1.238	135	167.1	
	4489	.2028	2.751	1.147	857	983.0	

4N. NH_4I. .048N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	752	.1942	2.811	1.205	582	701.3	
	1631	.2002	2.808	1.170	437	511.3	1.188
VI	3174	.1946	2.808	1.204	149	179.4	
	4443	.1974	2.805	1.188	870	1033.6	

4N. NH_4I.(Contd.)

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	701	.2032	2.717	1.170	560	655.2	
	1631	.2002	2.710	1.190	432	514.1	1.176
XII	3179	.1976	2.710	1.204	135	162.5	
	4490	.2028	2.705	1.177	857	1008.7	
(3)	718	.2001	2.860	1.178	562	662.0	
	1618	.2033	2.845	1.165	432	503.3	1.174
V	3182	.1997	2.845	1.186	136	161.3	
	4482	.2020	2.833	1.178	858	1010.7	

N. NaBr. .020N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	548	.2341	3.652	.770	448	345.0	
	1495	.2324	3.647	.776	403	312.7	.778
VI	3240	.....	.....	....	...	.....	
	4717	.2305	3.642	.784	775	607.6	
(2)	469	.2540	3.175	.801	340	272.3	
	1341	.2728	3.169	.747	372	277.9	.775
X	3242	.....	.....	....	...	.....	
	4948	.2626	3.164	.778	687	534.4	
(3)	355	.2913	2.839	.807	230	185.6	
	1208	.3122	2.836	.753	334	251.5	.777
I_a	3237	.....	.....	....	...	.....	
	5201	.3023	2.833	.779	598	465.8	

2N. NaBr. .033N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	424	.2669	2.991	.824	268	220.8	
	1269	.2936	2.987	.750	348	261.0	.772
VI	3200	.2134	2.983	1.034	15	15.6	
	5107	.2870	2.983	.768	631	484.6	

2N. NaBr.(Contd.)

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	381	.2814	2.959	.776	265	205.7	
	1290	.2876	2.950	.762	348	265.2	.763
X	3217	.2304	2.943	.953	15	14.3	
	5112	.2879	2.943	.763	628	479.2	
(3)	376	.2832	2.921	.781	259	202.3	
	1260	.2962	2.914	.748	345	258.0	.764
XII	3236	.....	.....	....	...	.....	
	5127	.2904	2.904	.765	623	476.6	

3N. NaBr. .043N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	516	.2418	3.846	.694	386	267.8	
	1433	.2481	3.840	.677	386	261.3	.680
VIII	3207	.2194	3.840	.766	48	36.7	
	4843	.2476	3.834	.680	724	492.3	
(2)	488	.2488	3.852	.674	395	266.3	
	1448	.2444	3.843	.688	389	267.5	.684
X	3239	.....	.....	....	...	.....	
	4825	.2453	3.835	.687	731	502.2	
(3)	498	.2462	3.914	.670	395	264.7	
	1462	.2406	3.907	.687	389	267.2	.676
XII	3218	.2320	3.907	.713	53	37.8	
	4822	.2448	3.900	.677	731	494.9	

4N. NaBr. .042N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	419	.2683	3.934	.623	297	185.0	
	1341	.2730	3.928	.614	359	220.4	.613
VI	3206	.2186	3.923		0		
	5034	.2757	3.923	.608	656	398.8	

4N. NaBr.(Contd.)

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	402	.2738	3.806	.614	292	179.3	
	1339	.2734	3.801	.615	357	219.6	.610
II_a	3208	.2203	3.795	.764	2	1.5	
	5051	.2780	3.795	.606	651	394.5	

N. NaI. .049N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	524	.2399	2.703	.986	373	367.7	
	1401	.2566	2.700	.923	382	352.5	.945
II_a	3206	.2186	2.700	1.084	41	44.5	
	4869	.2513	2.697	.944	714	674.0	
(2)	504	.2449	2.768	.994	340	338.0	
	1344	.2721	2.755	.899	372	334.4	.936
V	3201	.2142	2.755	1.142	25	28.5	
	4951	.2630	2.743	.934	687	641.6	

2N. NaI. .044N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	495	.2470	2.622	.997	347	345.9	
	1370	.2648	2.616	.932	374	348.5	.954
XII	3204	.2168	2.616	1.139	27	30.7	
	4931	.2600	2.610	.952	694	660.7	
(2)	532	.2379	2.671	1.017	363	369.1	
	1397	.2576	2.662	.942	379	357.0	.960
X	3176	.1960	2.662	1.238	35	43.3	
	4894	.2548	2.654	.955	707	675.2	

3N. NaI. .045N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	480	.2510	2.733	.942	366	344.7	
	1413	.2534	2.722	.937	380	356.1	.937
X	3220	.2345	2.722	1.012	38	38.5	
	4887	.2538	2.713	.938	708	664.0	
(2)	509	.2436	2.838	.934	393	367.1	
	1444	.2453	2.828	.931	388	361.2	.930
XII	3217	.2304	2.828	.991	52	51.6	
	4830	.2459	2.819	.932	729	679.4	

4N. NaI. .046N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	407	.2722	2.754	.904	304	274.8	
	1348	.2710	2.744	.912	361	329.2	.907
XI	3224	.2405	2.744	1.027	5	5.1	
	5021	.2734	2.736	.906	660	598.0	
(2)	480	.2511	2.875	.952	340	323.7	
	1373	.2641	2.873	.906	372	337.0	.919
V	3205	.2178	2.873	1.077	24	25.8	
	4942	.2618	2.869	.915	688	629.5	
(3)	510	.2433	2.774	.957	363	347.4	
	1385	.2608	2.766	.895	379	339.2	.918
XII	3210	.2224	2.766	1.050	35	36.8	
	4895	.2550	2.758	.918	707	649.0	

N. KBr. .022N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	378	.2824	2.729	.875	283	247.6	
	1316	.2803	2.724	.883	354	312.6	.881
V	3236	.2704	2.719	.917	7	6.4	
	5070	.2812	2.719	.882	644	568.0	

N. KBr.(Contd.)

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	410	.2712	2.743	.915	283	258.9	
	1296	.2860	2.741	.868	354	307.2	.885
III	3223	.2392	2.738	1.039	7	7.3	
	5071	.2813	2.738	.884	644	569.3	
(3)	428	.2657	2.754	.899	310	278.7	
	1341	.2730	2.751	.876	363	318.0	.883
IV	3222	.2378	2.751	1.006	9	9.1	
	5008	.2715	2.748	.882	664	585.6	

2N. KBr. .039N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	458	.2570	2.799	.898	350	314.3	
	1388	.2600	2.792	.890	373	332.0	.894
X	3229	.2502	2.792	.925	27	24.9	
	4925	.2592	2.785	.895	696	622.9	
(2)	475	.2523	2.835	.903	366	330.5	
	1408	.2548	2.828	.896	380	340.5	.900
XII	3229	.2502	2.828	.913	38	34.7	
	4888	.2540	2.822	.901	708	637.9	
(3)	447	.2600	2.756	.901	348	313.5	
	1402	.2564	2.751	.915	374	342.2	.904
VIII	3221	.2362	2.751	.993	28	27.8	
	4931	.2600	2.747	.904	694	627.4	

3N. KBr. .044N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	441	.2619	2.765	.892	326	290.7	
	1349	.2707	2.756	.867	368	319.0	.879
X	3231	.2546	2.756	.921	18	16.6	
	4979	.2670	2.747	.881	676	595.6	

3N. KBr.(Contd.)

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	411	.2708	2.783	.885	298	263.7	
	1341	.2730	2.781	.879	359	315.5	.874
I_a	3207	.2195	2.781	1.093	2	2.2	
	5046	.2766	2.779	.868	655	568.5	
(3)	442	.2615	2.793	.876	348	304.8	
	1413	.2534	2.790	.905	374	338.5	.885
II_a	3217	.2304	2.790	.995	28	27.8	
	4928	.2596	2.787	.884	694	613.5	
(4)	501	.2456	3.013	.889	370	328.9	
	1427	.2496	3.011	.875	381	333.4	.870
VI	3192	.2072	3.011	1.055	39	41.2	
	4880	.2528	3.009	.868	712	618.0	

4N. KBr. .045N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	369	.2858	2.735	.871	255	222.2	
	1268	.2940	2.732	.848	343	290.8	.851
III	3221	.2362	2.730	1.056	22	23.2	
	5143	.2930	2.730	.851	620	527.6	
(2)	407	.2722	2.758	.876	293	256.6	
	1320	.2790	2.752	.857	357	306.0	.863
IV	3223	.2392	2.748	1.001	1	1.0	
	5050	.2780	2.748	.861	651	560.6	

N. KI. .048N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	493	.2476	2.694	1.019	359	365.8	
	1394	.2584	2.690	.978	378	369.7	.989
VII	3207	.2195	2.690	1.151	33	38.0	
	4905	.2564	2.686	.987	704	694.8	

N. KI.(Contd.)

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	696	.2040	3.106	1.010	532	537.3	
	1576	.2130	3.099	.969	425	411.8	.988
II_a	3186	.2027	3.099	1.018	121	123.2	
	4542	.2090	3.094	.989	836	826.8	
(3)	715	.2008	3.159	1.037	525	544.4	
	1563	.2160	3.155	.965	423	408.2	.991
VI	3166	.1901	3.155	1.097	117	128.3	
	4556	.2107	3.151	.991	831	823.5	

2N. KI. .046N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	610	.2207	2.794	1.100	466	512.6	
	1532	.2236	2.789	1.088	408	443.8	1.083
IX	3186	.2027	2.789	1.200	86	103.2	
	4672	.2248	2.785	1.084	788	854.1	
(2)	640	.2146	2.764	1.089	492	535.8	
	1565	.2156	2.758	1.086	416	451.8	1.077
XII	3180	.1982	2.758	1.181	98	115.7	
	4616	.2177	2.752	1.078	810	873.2	

3N. KI. .045N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	630	.2164	2.692	1.145	485	555.3	
	1555	.2180	2.689	1.138	414	471.1	1.135
I_a	3190	.2057	2.689	1.206	94	113.3	
	4625	.2188	2.685	1.135	805	913.7	
(2)	671	.2087	2.716	1.161	506	587.5	
	1567	.2151	2.709	1.129	419	473.0	1.133
VI	3172	.1936	2.709	1.254	105	131.7	
	4591	.2149	2.702	1.133	820	929.1	

4N. KI. .046N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\overline{D}$.
(1)	684	.2062	2.792	1.182	528	624.0	
	1572	.2140	2.789	1.141	424	483.8	1.164
III	1395	.2095	2.789	1.165	118	137.5	
	4550	.2100	2.785	1.164	834	970.7	
(2)	742	.1960	2.749	1.199	560	671.4	
	1615	.2040	2.739	1.156	432	499.4	1.167
X	3157	.1856	2.739	1.271	135	171.6	
	4486	.2024	2.730	1.169	857	1001.8	

TABLE 2.

Ethylene Dibromide. .10N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	526	.2394	3.997	.710	422	299.6	
	1477	.2368	3.991	.719	396	284.7	.719
VII	3231	.2548	3.991	.668	65	43.4	
	4766	.2373	3.976	.720	753	542.2	
(2)	549	.2338	3.896	.709	443	314.1	
	1511	.2286	3.888	.726	402	291.8	.718
VIII	3217	.2304	3.888	.721	74	53.4	
	4722	.2312	3.882	.719	771	554.3	
(3)	553	.2329	3.863	.718	434	311.5	
	1506	.2300	3.849	.730	400	292.0	.719
X	3199	.2128	3.849	.789	72	56.8	
	4741	.2340	3.837	.720	762	548.6	

Acetylene Tetrabromide. .092N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	477	.2520	16.797	.1608	356	57.24	
	1390	.2595	16.778	.1563	377	58.92	.1581
III	3224	.2405	16.778	.1687	32	5.40	
	4909	.2569	16.761	.1581	701	110.83	
(2)	504	.2448	16.910	.1589	386	61.33	
	1436	.2472	16.895	.1575	386	60.79	.1570
VI	3212	.2245	16.895	.1735	48	8.32	
	4848	.2486	16.883	.1568	724	113.52	

Bromobenzene. .102N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	586	.2258	2.922	1.032	461	475.7	
	1525	.2252	2.917	1.036	407	421.6	1.035
III	3210	.2224	2.917	1.025	82	84.0	
	4679	.2257	2.913	1.035	786	813.5	

Bromobenzene,(Contd.).

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	603	.2220	2.934	1.035	480	496.8	
	1535	.2227	2.926	1.034	412	426.0	1.041
V	3218	.2320	2.926	..993	92	91.4	
	4644	.2214	2.919	1.043	800	834.4	
(3)	650	.2126	2.979	1.039	511	530.9	
	1569	.2147	2.972	1.031	420	433.0	1.038
VI	3202	.2150	2.972	1.030	109	112.3	
	4580	.2136	2.966	1.039	822	854.1	

Chloroform. .103N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	358	.2900	1.238	1.896	235	445.6	
	1255	.2977	1.233	1.855	335	621.5	1.836
III	3200	.2134	1.230	2.593	32	83.0	
	5188	.3004	1.230	1.843	602	1109.5	
(2)	378	.2824	1.203	1.954	230	449.4	
	1216	.3097	1.200	1.786	333	594.7	1.825
I	3209	.2214	1.197	2.505	36	90.2	
	5196	.3016	1.197	1.838	599	1101.0	

Carbon Tetrachloride. .093N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	692	.2049	2.726	1.156	560	647.4	
	1647	.1966	2.720	1.207	432	521.4	1.172
VIII	3172	.1936	2.720	1.226	135	165.5	
	4489	.2027	2.714	1.173	857	1005.3	
(2)	681	.2068	2.747	1.196	525	627.9	
	1605	.2062	2.743	1.202	423	508.4	1.181
VII	3163	.1887	2.743	1.313	117	153.6	
	4552	.2103	2.740	1.180	831	980.6	

Heptane. .088N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	468	.2543	1.100	2.384	370	882.1	
	1401	.2566	1.097	2.369	381	902.6	2.393
Ia	3250	.....	.....	.....	...	.....	
	4882	.2532	1.093	2.410	712	1715.9	
(2)	500	.2456	1.104	2.426	370	897.6	
	1409	.2546	1.101	2.347	381	894.2	2.373
IV	3215	.2282	1.101	2.618	39	102.1	
	4876	.2524	1.099	2.372	712	1688.8	
(3)	493	.2476	1.104	2.486	348	865.0	
	1375	.2635	1.101	2.343	374	876.3	2.392
VII	3207	.2195	1.101	2.812	28	78.7	
	4925	.2593	1.097	2.389	694	1657.9	

Benzene. .101N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	547	.2343	1.714	1.677	424	711.0	
	1478	.2366	1.708	1.668	396	660.5	1.667
V	3210	.2224	1.708	1.774	67	118.9	
	4765	.2371	1.702	1.670	753	1257.5	
(2)	622	.2183	1.701	1.772	436	772.6	
	1456	.2423	1.696	1.601	400	640.4	1.672
IV	3190	.2058	1.696	1.876	71	133.2	
	4732	.2326	1.692	1.672	765	1279.1	
(3)	631	.2165	1.740	1.789	436	780.0	
	1458	.2417	1.734	1.608	400	643.2	1.672
V	3173	.1942	1.734	2.002	71	142.1	
	4737	.2334	1.729	1.670	765	1277.6	

Toluene. .098N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	489	.2487	1.554	1.761	340	598.7	
	1357	.2684	1.550	1.636	372	608.6	1.685
III	3212	.2245	1.550	1.956	24	46.9	
	4942	.2616	1.545	1.684	688	1158.5	
(2)	557	.2318	1.609	1.730	416	719.7	
	1456	.2423	1.602	1.662	394	654.8	1.687
II	3206	.2186	1.602	1.842	63	116.0	
	4781	.2393	1.596	1.689	747	1261.7	

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m-Xylene. .092N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	407	.2722	1.676	1.462	310	453.2	
	1343	.2723	1.674	1.463	363	531.1	1.465
I_a	3240	.....	.....	.....	...	.....	
	5011	.2719	1.672	1.467	664	974.0	
(2)	463	.2556	1.747	1.473	347	511.1	
	1380	.2623	1.744	1.438	374	537.8	1.452
IV	3225	.2426	1.744	1.555	27	42.0	
	4931	.2600	1.741	1.453	694	1008.4	
(3)	443	.2613	1.773	1.467	328	481.1	
	1357	.2684	1.768	1.432	368	526.9	1.446
VII	3227	.2462	1.768	1.561	18	28.1	
	4974	.2663	1.765	1.446	678	980.4	

Anisole. .100N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	532	.2378	2.911	.950	434	412.3	
	1505	.2302	2.907	.983	400	393.2	.969
IV	3223	.2392	2.907	.946	72	68.1	
	4739	.2336	2.902	.970	762	739.1	

Anisole,(Contd.).

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	543	.2353	2.934	.976	430	419.7	
	1481	.2358	2.926	.977	398	388.8	.980
V	3225	.2426	2.926	.950	70	66.5	
	4751	.2353	2.919	.981	758	743.6	
(3)	555	.2323	2.966	.986	434	427.9	
	1481	.2358	2.962	.973	400	389.2	.983
VII	3225	.2426	2.962	.946	72	68.1	
	4739	.2336	2.957	.984	762	749.8	

Phenetole. .103N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	441	.2618	3.002	.837	334	279.5	
	1384	.2612	2.998	.840	370	310.8	.835
IV	3221	.2363	2.998	.929	20	18.6	
	4955	.2636	2.994	.834	684	570.4	
(2)	465	.2552	3.024	.873	340	296.8	
	1360	.2676	3.019	.834	372	310.3	.851
V	3226	.2441	3.019	.915	25	22.9	
	4949	.2627	3.013	.852	687	585.4	
(3)	512	.2429	3.035	.892	348	310.4	
	1379	.2624	3.033	.827	374	309.3	.843
VI	3183	.2006	3.033	1.081	28	30.2	
	4927	.2595	3.031	.836	694	580.1	

Acetic Acid. .094N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	550	.2336	3.004	.920	400	368.0	
	1466	.2395	2.998	.899	390	350.6	.890
VIII	3173	.1942	2.998	1.109	56	62.1	
	4811	.2434	2.992	.886	734	650.3	

Acetic Acid,(Contd.).

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	453	.2584	2.974	.883	347	306.4	
	1414	.2532	2.969	.902	374	337.3	.882
IX	3200	.2134	2.969	1.070	27	28.9	
	4932	.2602	2.965	.879	694	610.0	
(3)	521	.2406	2.951	.910	386	351.3	
	1440	.2463	2.946	.890	386	343.5	.889
XII	3199	.2128	2.946	1.030	48	49.4	
	4840	.2474	2.942	.887	724	642.2	

Methyl Alcohol. .095N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	522	.2403	1.614	1.738	328	570.0	
	1311	.2816	1.611	1.486	368	546.8	1.581
V	3187	.2034	1.611	2.057	18	37.0	
	4980	.2671	1.608	1.569	678	1063.7	
(2)	573	.2284	1.784	1.665	400	666.0	
	1400	.2568	1.780	1.484	390	578.8	1.563
IX	3209	.2214	1.780	1.721	55	94.7	
	4819	.2445	1.776	1.562	735	1148.1	

Ethyl Acetate. .106N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	666	.2096	1.744	1.862	519	966.3	
	1581	.2118	1.737	1.850	422	780.7	1.854
III	3188	.2042	1.737	1.919	114	218.7	
	4565	.2117	1.730	1.859	827	1537.4	
(2)	665	.2097	1.767	1.834	536	983.0	
	1606	.2060	1.762	1.873	426	797.9	1.864
VII	3204	.2168	1.762	1.779	122	217.0	
	4526	.2071	1.758	1.867	840	1568.3	

Amyl Acetate. .101N.I_2. 19.91°C.

	Propns.	X.	t.	D.	P.	DP.	$\overline{D}$.
(1)	641	.2143	2.839	1.108	470	520.8	
	1516	.2274	2.831	1.047	409	428.2	1.072
V	3190	.2056	2.831	1.158	88	101.8	
	4653	.2226	2.823	1.073	791	848.8	
(2)	678	.2073	2.753	1.132	480	543.4	
	1515	.2277	2.749	1.032	412	425.2	1.069
XII	3169	.1920	2.749	1.224	92	112.6	
	4637	.2204	2.744	1.068	800	854.4	

Carbon Bisulphide. .109N.I_2. 19.91°C.

(1)	428	.2657	.930	2.699	315	850.2	
	1379	.2625	.925	2.747	365	1002.6	2.697
I_a	3194	.2088	.925	3.453	11	38.0	
	5000	.2703	.920	2.682	669	1794.2	

Further Series of Experiments, performed in a Thermostatic Room.

With completion of the building of a thermo--static room, it became possible to perform experiments under the conditions recommended throughout the literature.

The room, which was double-walled and almost entirely below ground level, was lighted by means of an electric bulb which was well protected to prevent emission of heat. Changes of temperature in a night were not recorded on an ordinary Fahrenheit maximum and minimum thermometer.

A number of test experiments were performed with organic solvents. When the diffusion apparatus were placed directly in the room, experiments were not a success, owing to the slight rise of temperature due to the presence of the investigator. The tubes were next placed in heavy glass cylinders of water, whereby a great improvement was effected. Eventually they were inserted in a bath containing 150 litres of water at room temperature. This arrangement was the most satisfactory.

As at the higher temperature, the experiments were found to be very sensitive to temperature change, and sets of satisfactory results were obtained with great irregularity. Some solvents,- eg. heptane and m-xylene,- which yielded /

yielded good results, without trouble, at the higher temperature, now gave them with difficulty, although the bath temperature was seldom observed to vary by more than .1°C. in a day.

When experiments were successful, the temper--ature of the bath was usually very steady; when un--successful, there was frequently a slow rise or fall.

Latterly the time spent in the room was reduced to an absolute minimum. After fixing the tubes in the bath, they were left undisturbed for a few hours. The iodine solution was then run slowly into the tubes, as slow addition, under the new conditions of exper--iment, appeared to be an advantage. When three or four experiments had to be started the actual time spent in the room was frequently just five minutes,- one minute, or so, to turn on the stop-cocks, and short periods at intervals to turn them off.

On the whole, satisfactory results were obtain--ed more readily in the thermostatic room than in the thermostat.

The following table gives the results obtained. Further experiments have to be performed.

TABLE 3.

Bromobenzene. .096N.I_2. 8.82°- 8.80°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	399	.2748	2.828	.876	297	260.1	
	1333	.2753	2.822	.876	359	314.4	.875
III	3228	.2480	2.822	.973	1	1.0	
	5040	.2764	2.817	.874	655	572.5	
(2)	446	.2602	2.851	.870	347	301.9	
	1394	.2584	2.847	.877	374	328.0	.872
VIII	3227	.2462	2.847	.921	27	24.8	
	4933	.2603	2.844	.872	694	605.2	
(3)	446	.2602	2.864	.895	331	296.3	
	1370	.2648	2.860	.881	370	326.0	.882
Ia	3218	.2320	2.860	1.005	20	20.1	
	4966	.2651	2.858	.880	681	599.3	

Chloroform. .100N.I_2. 8.18°- 8.12°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	535	.2371	1.839	1.561	430	671.2	
	1498	.2317	1.836	1.600	398	636.8	1.576
III	3214	.2269	1.836	1.634	70	114.4	
	4753	.2355	1.832	1.578	758	1196.1	
(2)	552	.2331	1.859	1.568	443	694.6	
	1523	.2257	1.856	1.623	402	652.4	1.586
VII	3204	.2168	1.856	1.689	74	124.9	
	4722	.2312	1.853	1.586	771	1222.8	

Carbon Tetrachloride. .098N.I_2. 8.34°- 8.39°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	474	.2526	2.799	.963	379	364.9	
	1436	.2472	2.795	.985	384	378.2	.972
V	3225	.2426	2.795	1.004	45	45.2	
	4865	.2506	2.791	.973	718	698.6	

Carbon Tetrachloride, (Contd.).

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	487	.2490	2.841	.953	390	371.7	
	1458	.2416	2.833	.985	387	381.2	.965
V	3216	.2294	2.833	1.037	50	51.9	
	4838	.2470	2.827	.965	727	701.5	
(3)	489	.2486	2.851	.959	386	370.1	
	1447	.2445	2.847	.976	386	376.7	.963
VII	3218	.2320	2.847	1.029	48	49.4	
	4846	.2481	2.844	.963	724	697.2	

Carbon Bisulphide. .101N.I_2.

(1) 8.96°- 8.88°C.
(2) 8.96°- 8.88°C.
(3) 8.23°- 8.37°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	458	.2570	1.064	2.360	356	840.2	
	1417	.2524	1.059	2.415	377	910.5	2.383
VIII	3219	.2334	1.059	2.611	32	83.6	
	4906	.2566	1.054	2.387	701	1673.3	
(2)	438	.2627	1.083	2.344	348	815.7	
	1426	.2499	1.079	2.474	374	925.3	2.399
I_a	3216	.2294	1.079	2.695	28	75.4	
	4920	.2586	1.075	2.399	694	1664.9	
(3)	403	.2733	1.068	2.329	310	722.0	
	1356	.2686	1.062	2.383	363	865.0	2.362
VII	3234	.2620	1.062	2.443	9	22.0	
	5008	.2715	1.057	2.368	664	1572.3	

Heptane. .048N.I_2.

(1) 8.86°- 8.89°C.
(2) 8.98°- 8.90°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	459	.2567	1.250	2.121	322	682.9	
	1342	.2726	1.248	2.001	367	734.4	2.046
III	3214	.2268	1.248	2.405	16	38.5	
	4985	.2678	1.244	2.043	673	1374.9	
(2)	493	.2476	1.232	2.097	350	734.0	
	1391	.2593	1.224	2.015	376	757.7	2.034
II_a	3195	.2094	1.224	2.496	29	72.3	
	4921	.2587	1.217	2.032	697	1416.3	

Benzene. .102N.I_2.

(1) 8.86°C.
(2) 9.08°- 9.20°C.
(3) 8.04°- 8.18°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	565	.2301	1.980	1.492	386	575.9	
	1416	.2526	1.976	1.362	386	525.8	1.401
VII	3181	.1990	1.976	1.728	48	82.9	
	4839	.2472	1.972	1.394	724	1009.3	
(2)	585	.2259	2.013	1.497	395	591.3	
	1421	.2511	2.009	1.349	389	524.7	1.393
III	3173	.1940	2.009	1.747	53	92.6	
	4821	.2447	2.006	1.387	731	1013.9	
(3)	526	.2394	1.921	1.466	353	517.5	
	1368	.2655	1.917	1.324	377	499.1	1.376
V	3197	.2112	1.917	1.665	30	50.0	
	4910	.2570	1.913	1.371	700	959.7	

Toluene. .098N.I_2. 8.66°- 8.65°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	581	.2268	1.954	1.457	443	645.5	
	1491	.2333	1.951	1.418	402	570.0	1.432
VIII	3206	.2186	1.951	1.513	74	111.9	
	4722	.2312	1.949	1.432	771	1104.0	
(2)	555	.2323	1.972	1.456	426	620.2	
	1462	.2406	1.969	1.408	397	558.9	1.435
Ia	3224	.2404	1.969	1.409	67	94.3	
	4758	.2362	1.967	1.436	756	1085.6	

---

m-Xylene. .091N.I_2. (1) 8.86°- 8.91°C.
(2) 8.90°- 8.92°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	739	.1964	2.726	1.246	567	706.5	
	1628	.2010	2.723	1.219	433	527.8	1.222
Ia	3161	.1874	2.723	1.307	140	183.0	
	4472	.2007	2.719	1.222	860	1050.9	
(2)	757	.1934	2.762	1.272	567	721.2	
	1587	.2104	2.758	1.171	433	507.0	1.226
VII	3179	.1975	2.758	1.248	140	174.7	
	4476	.2012	2.753	1.227	860	1055.2	

Anisole. .096N.I_2. (1) 8.04°- 7.94°C.
(2) 8.08°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	366	.2868	3.000	.791	245	193.8	
	1225	.3069	2.997	.740	339	250.9	.765
III	3246	.....	.....	....	...	.....	
	5163	.2960	2.994	.768	611	469.3	

Anisole,(Contd.).

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(2)	491	.2480	3.604	.746	403	300.6	
	1459	.2414	3.600	.768	391	300.3	.760
Ia	3242	.....	.....	....	...	.....	
	4807	.2430	3.597	.763	737	562.3	

Phenetole. .097N.I_2. 8.08°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	416	.2693	3.684	.686	293	200.9	
	1294	.2865	3.677	.646	357	230.6	.665
III	3240	.....	.....	....	...	.....	
	5051	.2780	3.671	.667	651	434.3	
(2)	452	.2586	3.656	.719	280	201.3	
	1280	.2906	3.651	.641	353	226.3	.666
VII	3190	.2058	3.651	.906	8	7.2	
	5079	.2824	3.646	.660	641	423.1	

Methyl Alcohol. .093N.I_2. 8.91°- 8.93°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	560	.2311	2.024	1.380	391	539.6	
	1432	.2483	2.020	1.287	388	499.3	1.305
VIII	3174	.1947	2.020	1.641	51	83.7	
	4833	.2464	2.016	1.299	728	945.6	
(2)	572	.2286	2.040	1.460	363	530.0	
	1346	.2714	2.037	1.231	379	466.6	1.319
III	3185	.2020	2.037	1.654	35	57.9	
	4897	.2553	2.034	1.311	707	926.9	

Ethyl Acetate. .101N.I_2. 8.94°- 8.98°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	618	.2190	1.932	1.593	492	783.8	
	1559	.2170	1.924	1.614	416	671.4	1.609
V	3207	.2195	1.924	1.596	98	156.3	
	4616	.2178	1.916	1.615	810	1308.2	
(2)	604	.2220	1.886	1.623	470	762.8	
	1516	.2274	1.883	1.587	409	649.0	1.615
VII	3219	.2334	1.883	1.547	88	136.1	
	4661	.2235	1.881	1.617	791	1279.0	

Amyl Acetate. .103N.I_2. 8.94°- 8.99°C.

	Propns.	X.	t.	D.	P.	DP.	$\bar{D}$.
(1)	475	.2524	2.955	.913	331	302.2	
	1350	.2704	2.951	.853	370	315.6	.873
III	3205	.2177	2.951	1.060	20	21.2	
	4970	.2656	2.947	.870	681	592.5	
(2)	500	.2457	2.977	.899	348	312.8	
	1377	.2630	2.972	.842	374	314.9	.861
VI	3204	.2168	2.972	1.021	28	28.6	
	4919	.2584	2.967	.858	694	595.4	
(3)	513	.2426	3.010	.931	348	323.9	
	1363	.2667	3.005	.848	374	317.2	.879
VII	3203	.2159	3.005	1.048	28	29.3	
	4921	.2587	2.999	.876	694	607.9	

Determination of Density and Viscosity.

The following formula was used for the deter-
-mination of the absolute viscosity of the solvents and solutions employed.

$$z = \frac{s \cdot t}{s_o \cdot t_o} \cdot z_o$$

where z, and z_o are, respectively, the absolute coef-
-ficients of viscosity of the solvent and of a stand-
-ard liquid,- water or benzene, - s, and s_o are the densities of the same, and t, and t_o the times of flow in a capillary tube.

For the determination of density, pyknometers of 10 ccs. capacity, of the Sprengel-Ostwald[1] type were employed. The ends were protected by means of ground-glass caps.

Distilled water was used for determining the volumes of the pyknometers at the required temperatures. In all weighings buoyancy corrections were made.

The following values were taken for the density of water:-

8°C.	.....	·9999
10°C.	.....	·9997
12°C.	.....	·9995
19·9°C.	.....	·9982

For the measurement of the coefficients of vis-
-cosity, viscosity tubes of the Ostwald[1] type /

1) Ostwald-Luther, Physiko-Chemische Messungen.

type were chosen in accordance with the rules laid down by Findlay, (Practical Physical Chemistry,-Ch.V.).

A thermostat regulated to .02°C. and stirred with compressed air, was employed for obtaining values at the desired temperatures. The lower temperature work presented no difficulties.

Before use the various liquids were filtered through hardened filter paper, and placed in the bath to acquire the correct temperature. Viscosity deter--minations were then made in the customary manner. The measurements for each solvent and the corresponding iodine solution were preceded by standardisation of the viscosity tube with water or benzene,- benzene being frequently employed in the case of organic solvents. The time of outflow from the capillary was always found about five times, and the average taken. When values were irregular, the viscosity tube was thoroughly cleaned and the operation repeated..

The viscosity of benzene relative to that of water was experimentally found. Using Thorpe and Rodger's data for the viscosity of water, the absolute viscosity coefficients of the liquids were obtained.

Examples:-

a) The viscosity of 3N.NaBr, at 19.91°C. /

Examples:-

a) The viscosity of 3N.NaBr, at 19.91°C.

Density of 3N.NaBr..... 1·2279
Density of water..... ·9982
Absolute viscosity of water,(C.G.S. units).·01007
Time of flow in a capillary tube.

Water.	3N.NaBr.
184.6 secs.	190.4 secs.
184.7 "	190.6 "
184.5 "	190.45 "
184.6 "	190.6 "
184.4 "	190.5 "
184.8 "	190.4 "
Average: 184.6 "	190.49 "

$$z = \frac{190.49}{184.6} \cdot \frac{1.2279}{.9982} \cdot \frac{.01007}{1}$$

.01279 C.G.S. units.

b) The viscosity of Bromobenzene at 8.81°C.

Density of bromobenzene..... 1·5077
Density of benzene..... ·8900
Absolute viscosity of benzene,(C.G.S.uts.) ·00759
Time of flow in capillary tube.

274.2 secs.	278.6 secs.
274.3 "	278.4 "
274.6 "	278.7 "
274.0 "	278.2 "
274.2 "	278.5 "
Average: 274.26 "	278.48 "

$$z = \frac{278.48}{274.26} \cdot \frac{1.5077}{.8900} \cdot \frac{.00759}{1}$$

.01306 C.G.S. units.

Test of the Stokes-Einstein Equation.

In order to show the effect of varying viscos--ity of the solvent on the coefficient of diffusion of dissolved iodine, the product Dz was calculated. According to the Stokes-Einstein equation Dz ought to be constant. The following tables show whether or not this is so.

Tables 4 and 5 refer to the diffusion of iodine in aqueous solutions of bromides and iodides respec--tively, table 6 to diffusion in organic solvents at 19.91°C., and table 7 to diffusion in organic solvents at a temperature between 8°C. and 9°C.

In addition to the values of D, z, and Dz, there are given the densities of the solvents and iodine solutions, and the coefficients of viscosity of the latter.

Symbols used:-

a) Tables 4 and 5.

D - Average coefficient of diffusion, determined from the two or three mean values given in table 1.

s - Density of solvent.

s'- Density of iodine solution.

z - Viscosity of solvent in C.G.S. units, multi--plied by 10^5.

z'- Corresponding value for solution.

b) Tables 6 and 7. /

b) Tables 6 and 7.

The symbols referring to the higher temperatures are written thus - $\underline{D}_2$, $\underline{s}_2'$ etc., and to the lower temperature - $\underline{D}_1$ etc. In determining $\underline{D}_1$ for any solvent, it was necessary to bring all the mean values to the same temperature before taking the average. This was effected by using the temper--ature coefficient, calculated from the high temp--erature value and a low temperature value.

Table 4.

Temperature throughout,- 19.91°C.

Solvent	s.	s!	z	z'	D.	Dz
N.NH_4Br	1.0527	1.0558	964	969	.883	851
2N.NH_4Br	1.1058	1.1107	935	942	.910	851
3N.NH_4Br	1.1582	1.1630	927	934	.922	855
4N.NH_4Br	1.2109	1.2156	934	939	.889	830
N.NaBr	1.0765	1.0799	1063	1064	.777	826
2N.NaBr	1.1526	1.1559	1144	1151	.766	876
3N.NaBr	1.2279	1.2320	1279	1284	.680	870
4N.NaBr	1.3021	1.3085	1459	1473	.612	893
N.KBr	1.0818	1.0839	962	967	.883	849
2N.KBr	1.1631	1.1670	947	950	.899	851
3N.KBr	1.2438	1.2478	951	957	.877	834
4N.KBr	1.3230	1.3267	974	980	.857	835

Table 5.

Temperature throughout,- 19.91°C.

Solvent.	s	s'	z	z'	D	Dz
N.NH_4I	1.0888	1.0950	927	931	.995	922
2N.NH_4I	1.1783	1.1843	875	880	1.095	958
3N.NH_4I	1.2707	1.2740	862	867	1.146	988
4N.NH_4I	1.3573	1.3611	863	868	1.179	1017
N.NaI	1.1128	1.1166	1021	1025	.941	961
2N.NaI	1.2253	1.2281	1073	1077	.957	1027
3N.NaI	1.3355	1.3402	1174	1184	.934	1097
4N.NaI	1.4444	1.4514	1329	1342	.915	1216
N.KI	1.1178	1.1234	926	933	.989	916
2N.KI	1.2343	1.2381	900	904	1.080	972
3N.KI	1.3519	1.3563	891	896	1.134	1010
4N.KI	1.4683	1.4724	906	910	1.166	1056

Table 6.

Temperature throughout - 19.91°C.

Solvent.	S_2	S'_2	z_2	z'_2	D_2	$D_2 z_2$
Ethylene Dibromide	2.1705	2.1780	1714	1720	.719	1232
Acetylene Tetrabromide	2.9536	2.9578	9797	9724	.1576	1544
Bromobenzene	1.4944	1.5028	1133	1138	1.038	1176
Chloroform	1.4850	1.4930	580	585	1.831	1062
Carbon Tetrachloride	1.5933	1.6002	958	961	1.177	1128
Carbon Bisulphide	1.2630	1.2729	376	377	2.697	1014
Heptane	.7167	.7281	481	484	2.386	1148
Benzene	.8784	.8883	642	648	1.670	1072
Toluene	.8682	.8779	582	588	1.686	981
m-Xylene	.8620	.8719	643	649	1.454	935
Anisole	.9939	1.0037	1081	1089	.977	1056
Phenetole	.9692	.9792	1318	1330	.843	1111
Acetic Acid	1.0501	1.0593	1253	1266	.887	1111
Methyl Alcohol	.7931	.8047	611	619	1.572	960
Ethyl Acetate	.8996	.9116	457	464	1.859	850
Amyl Acetate (iso-)	.8712	.8817	872	884	1.071	933

Table 7.

Solvent.	Temp.	s,	s',	z,	z',	D,	D,z,
Bromobenzene	8.81°	1.5077	1.5155	1306	1309	.876	1144
Chloroform	8.10°	1.5039	1.5151	643	646	1.581	1017
Carbon Tetrachloride	8.37°	1.6152	1.6225	1140	1142	.967	1102
Carbon Bisulphide	8.92°	1.2790	1.2883	408	411	2.387	974
Heptane	8.91°	.7280	.7328	546	550	2.039	1113
Benzene	8.86°	.8900	.9012	758	765	1.394	1057
Toluene	8.66°	.8784	.8885	667	675	1.434	956
m-Xylene	8.90°	.8712	.8809	734	745	1.224	898
Anisole	8.08°	1.0045	1.0140	1309	1317	.763	999
Phenetole	8.08°	.9786	.9884	1610	1620	.666	1072
Methyl Alcohol	8.92°	.8049	.8156	711	731	1.312	933
Ethyl Acetate	8.96°	.9138	.9239	516	524	1.612	832
Amyl Acetate(iso-)	8.97°	.8828	.8932	1030	1045	.871	897

DISCUSSION OF RESULTS.

In tables 1 - 3 it is noted that the maximum variation of D for any one set of experiments is 2%. In most cases the variation is 1% or less. It may be assumed, therefore, that D was determined with fair accuracy.

The D values given by Euler[1] for the diffusion of iodine in benzene, at 12°, and in carbon bisulphide, at 16°, are 1.41 and 2.55 respectively. Recalculated to 20° they are slightly lower than those just tabu-lated.

The viscosity determinations of the organic solvents show fair agreement with the values given in the Landolt-Börnstein Tabellen. For the salt solutions the determinations are in good agreement with those found by Ranken and Taylor[2], and Getman[3]. z was most probably obtained with 1% accuracy.

1) Wied.Ann. 63, 273(1897).

2) Proc.Roy.Soc.Edin. 25, 231(1904).

3) Jour.Amer.Chem.Soc. 30, 722(1908).

Organic Solvents.

The Stokes-Einstein Equation.

It is obvious that tables 6 and 7 do not in--dicate the constancy of Dz required by the Stokes-Einstein equation. At the higher temperature, D_2z_2 varies within the wide limits 850 and 1544, a range far in excess of the experimental error; at the lower temperature, D_1z_1 varies in an analogous manner, but the values are roughly 3% lower.

Despite this, the viscosity of the solvent appears to play an important part in regulating the speed of diffusing molecules. Thus, in the eight cases where D_2z_2 lies between 1014 and 1148, z_2 varies bet--ween 376 and 1318.

Nature of Variation of Dz at constant temperature.

In the first place, owing to the considerable dilution of the iodine solutions, inconstancy of Dz cannot be attributed to different degrees of change in the viscosities of the pure solvents. z' and z differ, in general, by about 1%, the difference being probably slightly greater for the esters and methyl alcohol. Öholm used concentrated solutions and had to take into account the viscosities of the solutions in calculating Dz.

It must next be found if Dz bears any relation to some physical property of the solvent. The follow--ing tables show how Dz and D vary with M, the mole--cular weight, s, the density, V ($=\frac{M}{s}$), the molecular volume, E, the dielectric constant, and z, the vis--cosity of the solvent.

In table 8, the solvents are arranged in order of increasing values of Dz, and in table 9, solvents of similar constitution are bracketed together.

Table 8.

Solvent.	Dz.	D.	M.	s.	V.	z.	E.
Ethyl Acetate	850	1.859	88	.900	98	457	6.3
Amyl Acetate(iso-)	933	1.071	130	.871	149	872	4.8
m-Xylene	935	1.454	106	.862	123	643	2.4
Methyl Alcohol	960	1.572	32	.793	40	611	32.0
Toluene	981	1.686	92	.868	106	582	2.3
Carbon Bisulphide	1014	2.697	76	1.263	60	376	2.6
Anisole	1056	.977	108	.994	109	1081	4.4
Chloroform	1062	1.831	120	1.485	81	580	5.0
Benzene	1072	1.670	78	.878	89	642	2.3
Acetic Acid	1111	.887	60	1.050	57	1253	9.7
Phenetole	1111	.843	122	.969	126	1318	-
Carbon Tetrachloride	1128	1.177	154	1.593	97	958	2.3
Heptane	1148	2.386	100	.717	140	481	1.9
Bromobenzene	1176	1.038	157	1.494	105	1133	5.2
Ethylene Dibromide	1232	.719	188	2.171	87	1714	4.8
Acetylene Tetrabromide	1544	.1576	346	2.954	117	9797	7.1

Table 9.

Solvent.	Dz.	D.	M.	s.	V.	z.	E.
Bromobenzene	1176	1.038	157	1.494	105	1133	5.2
Ethylene Dibromide	1232	.719	188	2.171	87	1714	4.8
Acetylene Tetrabromide	1544	.1576	346	2.954	117	9797	7.1
Chloroform	1062	1.831	120	1.485	81	580	5.0
Carbon Tetrachloride	1128	1.177	154	1.593	97	958	2.3
Benzene	1072	1.670	78	.878	89	642	2.3
Toluene	981	1.686	92	.868	106	582	2.3
m-Xylene	935	1.454	106	.862	123	643	2.4
Anisole	1056	.977	108	.994	109	1081	4.4
Phenetole	1111	.843	122	.969	126	1318	-
Ethyl Acetate	850	1.859	88	.900	98	457	6.3
Amyl Acetate(iso-)	933	1.071	130	.871	149	872	4.8
Carbon Bisulphide	1014	2.697	76	1.263	60	376	2.6
Heptane	1148	2.386	100	.717	140	481	1.9
Methyl Alcohol	960	1.572	32	.793	40	611	32.0
Acetic Acid	1111	.887	60	1.050	57	1253	9.7

It appears, from the first of the tables, that there is no regularity in the change of Dz with change in any one of the given properties of the solvent. When, however, the separate groups are considered in table 9, it is found that,

1) As M and V increase, Dz increases, save in the case of the aromatic hydrocarbons.
2) As E increases, Dz decreases, except for the bromo compounds.
3) As s increases, Dz increases for the first three sets, but decreases for the two sets in which the solvents contain oxygen.
4) As D decreases and z increases, Dz, in general, increases.

Referring to any one solvent property, Dz does not vary in the same direction in all the groups of solvents, and, further, the relative rates of change in the different groups are very dissimilar. Öholm's and Thovert's results also show that, if a few solvents be arranged in order of increasing Dz values for a certain solute, the order is not necessarily the same for another solute.

The condition of the dissolved iodine must be considered, as the radius of the diffusing molecule comes into the Stokes-Einstein equation.

Iodine solutions have been frequently studied in order to /

in order to find in what way the iodine in a brown solution differs from that in a violet solution. Loeb[1] assumed that the iodine in brown solutions is present as I_4, and in the violet solutions as I_2, and that, under any particular set of conditions, there is a state of equilibrium, $I_4 \rightleftharpoons 2I_2$, which regulates the tint of the solution. Beckmann[2] and his co-workers found, however, that Loeb's hypothesis is wrong, and that the molecular weight in all solutions is near that required by I_2. On account of this, they assumed partial combination of solvent and solute, with for-mation of a compound SI_2. Under given conditions there is a balanced reaction $SI_2 \rightleftharpoons S + I_2$. Subsequent investigations have lent support to this theory. One might therefore expect to find some connection between Dz and the colour of the iodine solutions.

Small tubes containing decinormal solutions of iodine in the various solvents were arranged in order of colour, from blue-purple to brown, and the order found was as follows. Dz values are given alongside.

1) Zeit.für.phys.Chem. 2, 606(1888).

2) Zeit.für.phys.Chem. 17, 107(1895); 58, 543(1907).

Table 10.

Solvent.	Colour of I_2 solution.	Dz
Carbon Tetrachloride	Blue-purple.	1128
Heptane		1148
Carbon Bisulphide	Red-purple.	1014
Chloroform		1062
Acetylene Tetrabromide		1544
Bromobenzene	Red.	1176
Benzene		1072
Toluene	Red with	981
m-Xylene	tinge of	935
Ethylene Dibromide	brown.	1232
* Phenetole		1111
* Anisole	Deep brown.	1056
Acetic Acid		1111
Amyl Acetate (iso-)		933
* Ethyl Acetate	Brown.	850
Methyl Alcohol		960

* Order uncertain.

Considering the table as a whole there is little connection between Dz and the colour of the iodine solutions. In a brown solution one expects to find Dz smaller owing to greater combination of solute and solvent, and consequent increase in size of the dif--fusing molecule.

On once more grouping together the solvents of similar nature it is found that there is a decrease in Dz in agreement with the colour change in passing from ——

1) Carbon Tetrachloride to Chloroform.

2) Acetylene Tetrabromide to Ethylene Dibromide.

3) Benzene to Toluene.

4) Toluene to m-Xylene.

For the other two sets, the order was too uncertain to enable conclusions to be drawn.

Variation in Dz might be due to non-fulfilment of the condition required by Stokes' Law, that the solvent molecules must be small compared with those of the solute.

According to Sutherland[1], Dz should assume a higher value as the solvent molecules increase in size with respect to the molecules of a given solute. Thus, in the extreme case of a small molecule moving amongst larger solvent molecules, he supposes that the former travels more or less in the gaps which would be left, if the solvent molecules were forced almost into per--manent contact with each other. Where this "slipping" is a maximum he represents D by the formula-

$$D = \frac{RT}{N} \cdot \frac{1}{4\pi zr}$$

The other extreme case, where the "slipping" is nil is represented by the ordinary Stokes-Einstein equation.

A further scrutiny of tables 6 and 7, if the bromo compounds be omitted, fails to reveal a distinct difference between the values of Dz in solvents which may be considered to have large molecules and in those where /

1) Phil. Mag. (6) 9, 781(1905).

where the molecules are supposed to be small. The high values obtained when iodine diffuses in bromo com -pounds are probably due to the bromine. With regard to this the following points are of interest.

In estimating the diffusion coefficients of organic substances in water, methyl alcohol and benzene for the purpose of testing the relation $\underline{MD}^2$ = a constant, Thovert [1] found that compounds containing halogens give, in general, a value of $\underline{MD}^2$ somewhat higher than that obtained for a large range of alcohols, phenols, etc. A study of his tables shows that, in chloro compounds, the effect is less than in bromo and iodo compounds. In similarly constituted bromo com-pounds $\underline{MD}^2$ usually increases with increase in the a-mount of bromine.

Öholm [2] likewise drew attention to the fact that the introduction of the halogens into aliphatic and aromatic organic compounds usually increases their diffusibility, the effect being greatest for iodine and least for chlorine,

Iodine itself gives, in methyl alcohol and ben-zene solutions, a value of $\underline{MD}^2$ comparable with the highest values found by Thovert.

1) Ann.de Phys. 2, 421(1914).

2) Meddel.Nobelinst. 2, Nr.24, 26(1913).

The abnormally high Dz values for iodine dif--fusing in bromo compounds seem to depend on the amount of bromine and probably on its nature of com--bination with the rest of the solvent molecule. The close chemical relation between bromine and iodine may also affect the diffusibility of the latter. It would be interesting to find if other solutes give normal Dz values in solvents containing a large per--centage of bromine or iodine.

Variation of Dz with Absolute Temperature.

If, in the Stokes-Einstein equation, r be as--sumed constant at two temperatures T_2 and T_1 the following relation is derived:-

$$D_2 z_2 / D_1 z_1 = T_2 / T_1$$

where T_2 and T_1 are absolute temperatures.

In table 11 the ratios $D_2 z_2 / D_1 z_1$ and T_2 / T_1 are given for the thirteen solvents of table 7.

Table 11.

Solvent.	D_2z_2/D_1z_1.	T_2/T_1.
Bromobenzene	1.028	1.039
Chloroform	1.044	1.042
Carbon Tetrachloride	1.024	1.041
Carbon Bisulphide	1.041	1.039
Heptane	1.031	1.039
Benzene	1.014	1.039
Toluene	1.026	1.040
m-Xylene	1.041	1.039
Anisole	1.058	1.042
Phenetole	1.036	1.042
Methyl Alcohol	1.029	1.039
Ethyl Acetate	1.022	1.039
Amyl Acetate(iso-)	1.040	1.039

D_2z_2/D_1z_1 is found, on the whole, to be slightly less than T_2/T_1. Thus, in eight cases it is undoubtedly less, in four , almost the same, and, in the remaining, is decidedly higher. Taking the average, D_2z_2/D_1z_1 is 1.033, and T_2/T_1 1.040.

Cohen and Bruins[1] found that, for a temperature difference of 50°, D_2z_2/D_1z_1 was 3% lower than T_2/T_1, when tetrabromethane diffused in tetrachlorethane. The average values, above, show a similar difference, which may, however, be a coincidence, as the experimental results are not sufficiently accurate to prove that there is a difference.

1) Zeit. für phys. Chem. 103, 404(1923).

The Temperature Coefficient of Diffusion.

From the values of D_2 and D_1 at the higher and lower temperatures, T_2 and T_1, the temperature coefficients of diffusion, α, were calculated by means of Nernst's formula:-

$$D_2 = D_1 (1 + \alpha \overline{T_2 - T_1}).$$

The α values are given in the following table, where the solvents are arranged in order of increasing diffusibility of the dissolved iodine.

Table 12.

Solvent.	D_1 - D_2	α
Phenetole	.666 - .843	.023
Anisole	.763 - .977	.024
Amyl Acetate(iso-)	.871 - 1.071	.021
Bromobenzene	.876 - 1.038	.017
Carbon Tetrachloride	.967 - 1.177	.019
m-Xylene	1.224 - 1.454	.017
Methyl Alcohol	1.312 - 1.572	.018
Benzene	1.394 - 1.670	.018
Toluene	1.434 - 1.686	.016
Chloroform	1.581 - 1.831	.013
Ethyl Acetate	1.612 - 1.859	.014
Heptane	2.039 - 2.386	.016
Carbon Bisulphide	2.387 - 2.697	.012

α appears to depend, to a certain extent, on D, decreasing as the latter increases. Öholm's results also indicate this relation.

Aqueous Salt Solutions as Solvents.

The Variation of Dz.

There is an essential difference in the Dz values obtained from tables 4 and 5. While Dz for bromides never differs much from the mean,- 850(approx), Dz for iodides increases with increasing normality of the dissolved salts. The values are also much higher than for bromides, and sodium iodide gives the highest results.

The variable nature of Dz in table 5 is not attributable to experimental error, nor, in all pro--bability, is the increase of Dz in table 4 for sodium bromide.

Graphs were drawn in order to compare the variation of D with the variation in the fluidity, or inverse viscosity, F, of the solvent.

Since Dz in table 4 is fairly constant it was assumed that the value of Dz for water was 850 and that D was .85. Using this latter value all the dif--fusion constants were recalculated with reference to that for water as 1.00. The fluidities were also calculated.

Graphs A and B (pp. 86 and 87) show how D and F vary with the normality of the bromide and iodide solutions respectively. Values /

Values of D and F are plotted on the same graph for ready comparison. The different effects of bromides and iodides on the rate of diffusion of dissolved iodine are clearly illustrated.

Graphs C (p.88) were drawn to show how Dz varies with the normality, and with the percentage concentra--tion of the iodide solutions.

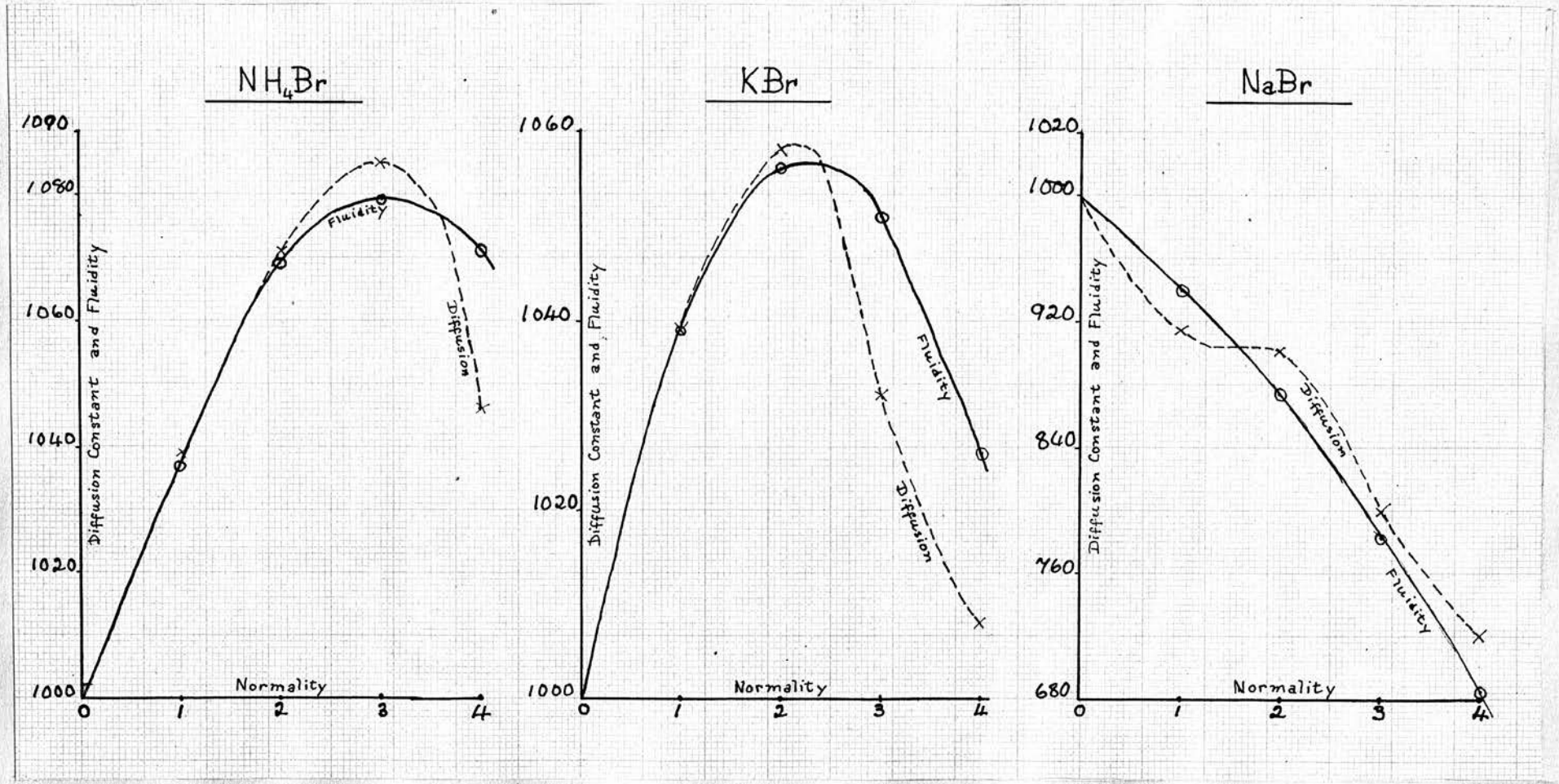
While, for the potassium and ammonium salts, Dz shows almost a linear relation with normality, for sodium iodide it appears to increase more rapidly in the more concentrated solutions.

Edgar and Diggs[1] found that, at 25°, the dif--fusion constants of .05N iodine in 1,2,3 and 4.5N potassium iodide solutions are 1.195, 1.260, 1.280 and 1.280. When these are multiplied by the corres--ponding viscosity coefficients of the solvents the following values of Dz are obtained:-

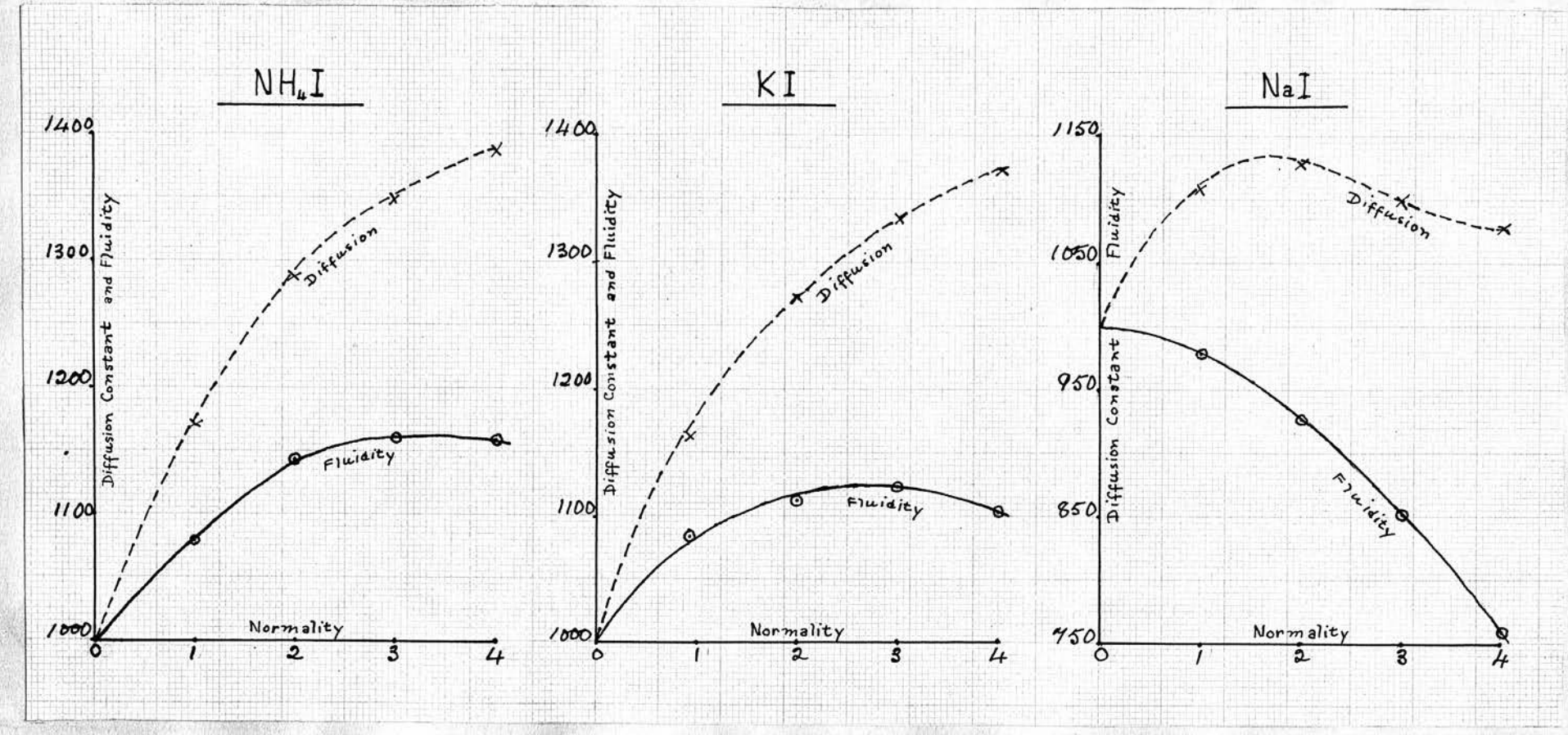
1020, 1055, 1074, 1123.

These results, compared with those just ob--tained, indicate that Dz increases considerably with rising temperature, and that the rate of increase probably depends on the amount of dissolved salt.

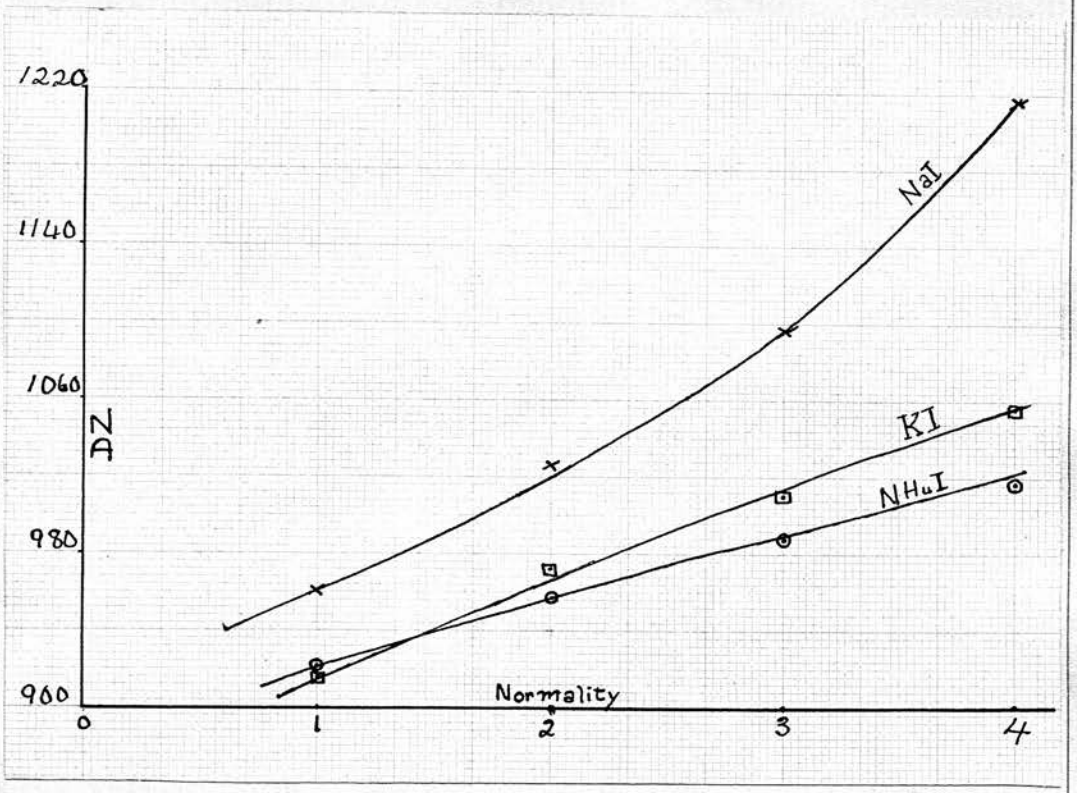
1) Jour.Amer.Chem.Soc. 38, 253(1916).


NH4Br
1090
1080
1060
1040
1020
1000
Diffusion Constant and Fluidity
Fluidity
Diffusion
Normality
0
1
2
3
4
KBr
1060
1040
1020
1000
Diffusion Constant and Fluidity
Fluidity
Diffusion
Normality
0
1
2
3
4
NaBr
1020
1000
920
840
760
680
Diffusion Constant and Fluidity
Diffusion
Fluidity
Normality
0
1
2
3
4

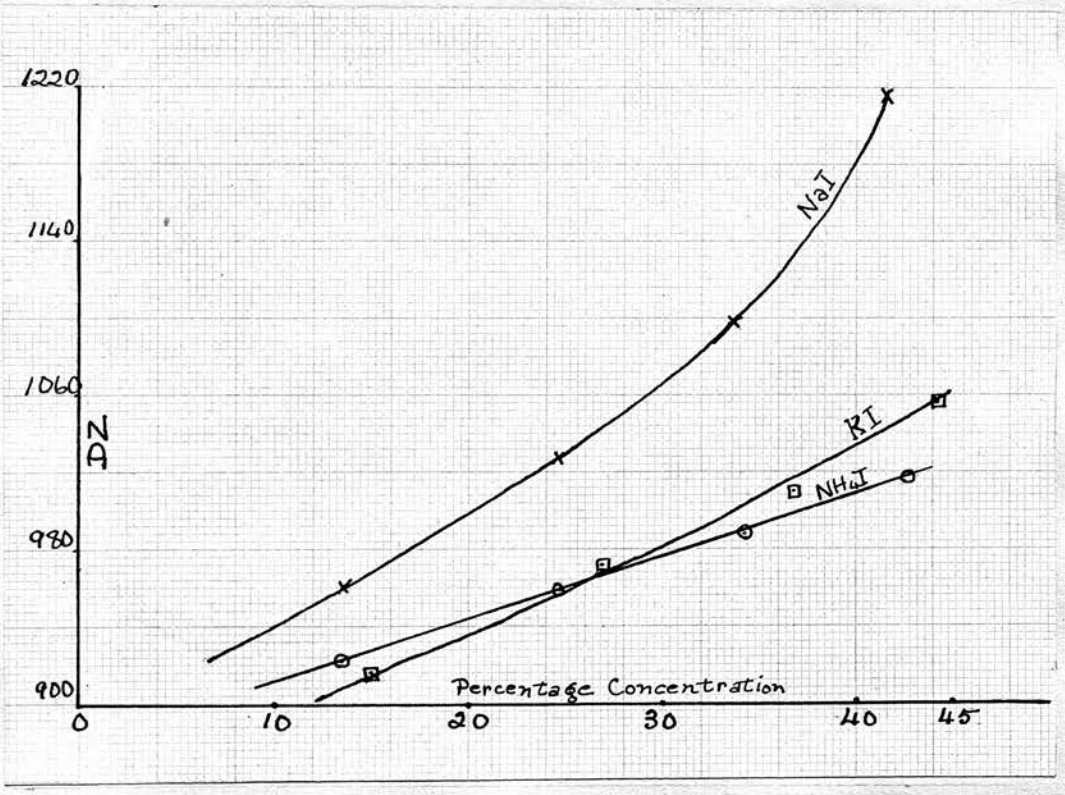
Graphs A


NH4I
KI
NaI
Diffusion Constant and Fluidity
Diffusion
Fluidity
Normality
1400
1300
1200
1100
1000
1150
1050
950
850
750
0
1
2
3
4

Graphs B


1220
1140
1060
980
900
DZ
NaI
KI
NHuI
Normality
0
1
2
3
4

Graphs C


1220
1140
1060
980
900
DZ
NaI
KI
NHuI
Percentage Concentration
0
10
20
30
40
45

The Influence of Iodides on the Rate of Diffusion of Dissolved Iodine.

Leblanc and Noyes[1], Jakowkin[2], Dawson[3] and others have found that, in solutions of alkali iodides, iodine exists mainly as the triiodide XI_3, if X is the metallic radicle. Dawson, moreover, shows that, even for a solution of iodine less than .05N, the amount of free iodine in a .25N solution of potassium iodide is less than 1%.

If the above conclusions are correct, it may be assumed that, in the concentrated solutions used for the diffusion experiments, there was no free iodine present and that the diffusing elements were XI_3 and its ions $X^{\cdot}$ and $I_3^{\prime}$.

In the following discussion the expressions "decrease" and "increase" of the diffusion constant refer to changes, apart from those due to increasing or decreasing viscosity of the solvent. Such changes are made evident by variations of Dz. Thus, although the actual rate of diffusion of iodine in 4N sodium iodide solution is less than that in the 1N solution, the /

1) Zeit.für.phys.Chem. 6, 385(1890).

2) Zeit.für.phys.Chem. 13, 539(1894); 20, 19(1896).

3) Jour.Chem.Soc. 79, 238(1901).

the former would be greater than the latter if the viscosities of the two solutions were identical. On this basis, the diffusion constant of dissolved iodine increases with increase in concentration of the dis--solved halide.

Since the diffusion constant of an undissocia--ted molecule is, in general, less than that of its component ions, one would expect the diffusion con--stant of XI_3 and its ions to decrease with increase in the amount of dissolved halide, owing to reduction of the degree of ionisation by the large excess of a common ion. This is not so.

Arrhenius[1] found that the diffusion constants of strong acids and bases in solutions of their salts are much greater than in water. He attributed it to the fact that the force,— due to the electrical pot--ential difference,—which resists the diffusion of $H^{\cdot}$ or OH' is spread over a greater number of ions, there--by increasing the diffusibility of $H^{\cdot}$ and OH'. In a similar fashion, the rate of diffusion of the other ionic constituent of the acid or base should be re--tarded.

Abegg and Bose[2] later deduced theoretically that /

1) Zeit.für phys.Chem. 10, 51(1892).

2) Zeit.für phys.Chem. 30, 545(1899).

that when an electrolyte diffuses in a large excess of its cation the speed of diffusion approaches that of its anion, and vice versâ. Since the migration velo--cities of $Na^{\cdot}$, $K^{\cdot}$ and $NH_4^{\cdot}$ exceed that of I_3' the dif--fusion constant of XI_3 and its ions should be dimin--ished in the presence of XI. This is not the case.

It appears that the phenomena connected with the diffusion of iodine in solutions of XI cannot be explained by simply considering the electrolytic effects produced by dissociation of XI_3 and of XI.

Parsons[1] thought that there are no complexes formed between iodine and potassium iodide. Since Abegg and Hamburger[2] showed that iodine is very soluble in potassium iodide itself, giving a solution, liquid at 82°, Parsons explained the high solubility of iodine in aqueous potassium iodide solutions as being due to its "solution in a dissolved solid".

Now, Bell and Buckley[3] concluded that iodine can only combine to a very slight extent with sodium and potassium bromides in aqueous solutions, hence, since Dz for bromides is fairly constant one might expect to find Dz for iodides more nearly constant than it is, if Parsons' conception be correct.

1) Jour. Phys. Chem. 11, 659(1907).

2) Zeit.für anorg. Chem. 50, 403(1906).

3) Jour. Amer. Chem. Soc. 34, 10(1912).

The process of diffusion of one substance in the solution of another is evidently very complicated. It has not been studied to any great extent with dil--ute solutions of the diffusing substance.

Employing fairly concentrated solutions, Thovert[1] investigated the diffusion, not only of elec--trolytes in solutions of electrolytes, but of electro--lytes and non-electrolytes in solutions of non-elec--trolytes. Using a two-layer system he found that, as the diffusing substance passed upwards, there was a displacement upwards or downwards of the additional solute. His results serve to show that there are forces at work independent of those connected with the pheno--mena of electrolytic dissociation.

Osborne and Jackson[2] observed that, when dex--trose or ammonium sulphate diffuse in a .1N solution of sodium chloride, the concentration of the latter increases in the upper layer.

If we suppose that iodine is present as XI_3 in a solution of XI, then, in all probability, we have to deal with the diffusion of XI_3 and XI. Since the dif--fusion constant of XI_3 increases with the amount of XI added, it is highly probable that XI diffuses down--wards, "pushing up" the XI_3 and giving a greater concentration of XI in the lower layers.

1) Ann.de Phys. 2, 405(1914).

2) Biochem.Jour. 8, 246(1914).

CONCLUSION.

Owing to the complex nature of solutions the Stokes-Einstein equation does not appear to be appli-cable to the process of diffusion therein. This is not altogether unexpected, as the law of Stokes is based on simple suppositions which are rarely fulfilled. where ordinary dissolved molecules are concerned.

Further, in considering the diffusion of the dissolved substance only, and neglecting that of the solvent itself, the whole process of diffusion is being regarded in a very one-sided manner. Even when a dilute solution is placed in contact with the pure solvent the heterogeneity of the system causes both solvent and solute to diffuse. Owing to the conditions of equilibrium of the liquid state their diffusibilities become equalised, but movement takes place in opposite directions.[1]

In a three component system, however, when the solvent itself is a solution of another substance, the displacements of two components are, to a certain extent, independent and they regulate the movement of the third. The essential independence of molecular movement is well marked in these ternary mixtures.

It is not surprising that little progress has been made in finding a definite relation between the diffusion constant and other molecular properties.

1) Jellinek, - Lehrb.d.Phys.Chem. Vol.2, p.882.

SUMMARY.

1) It was proposed that diffusion experiments be per-formed in order to test the applicability of the Stokes-Einstein equation.

2) Under certain conditions, a thermostat was found to be a satisfactory constant-temperature medium in which to perform diffusion experiments. Later, a thermostatic room was found to be, on the whole, more suitable.

3) The rate of diffusion of iodine -D- was found in numerous organic solvents, and in various solutions of alkali bromides and iodides. In addition, the viscosity coefficients -z- of the solvents were determined.

4) The Stokes-Einstein equation was tested by finding whether or not the product Dz was constant for the various solvents.

5) From the inconstancy of Dz, and taking into account the work of previous experimenters, it appeared that the Stokes-Einstein equation is not applicable to the diffusion of ordinary dissolved molecules.

6) Attempts were made to account for the variability of Dz and to find if the latter depended, in any way, on properties of the solvents.

7) It was concluded that Stokes' Law cannot be app-lied to dissolved molecules, that the process of diffusion is very complicated, and that probably the /

the complications are, in part, due to the down--ward diffusion of the solvent, or to upward or downward displacement of its constituents, if the diffusion medium is a solution of another sub--stance.
